

ENAMELS

The Preparation, Application, and Properties of
Vitreous Enamels

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BY ANDREW L. ANDREW

ENDORSEMENTS

The Fellows of The American Ceramic Society commend this book as a substantial contribution to an important technical and industrial field in which there has been a dearth of comprehensive and constructive literature.

The Porcelain Enamel Institute has encouraged the writing and publication of this book in an effort to further the knowledge and promote research and development in the field of porcelain enameling. Having been approved by its technical committee and the Educational Bureau of the Institute, it is recommended as a valuable contribution to the technology of the porcelain enamel industry.

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The Preparation, Application, and
Properties of Vitreous Enamels

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PREFACE

The primary motive underlying the preparation of this book has been the presentation of the technology of enameling in a systematic manner, suitable to the needs of both the industrial man and the student. To that end, an attempt has been made to summarize the literature, together with the author's experience.

The term enamel, as used in this book, refers to a thin layer of glass fused onto the surface of a metal. Although the terms *porcelain enamel* and *vitreous enamel* are sometimes used, the simpler term was selected because of its historical significance. It must not be confused, however, with the glossy paints which are sometimes called enamels.

For many years enameling was shrouded in secrecy, but the application of chemistry, physics and engineering has changed that condition. Technical societies, especially the American Ceramic Society, have done much toward the development of co-operation and have aided greatly in the publication of papers on the subject. The formation of the Porcelain Enamel Institute and its association with the Fellows of the American Ceramic Society in encouraging the writing of this book are evidence of the co-operative spirit which now exists.

The author wishes to thank the officers and members of the Porcelain Enamel Institute and the Fellows of the American Ceramic Society for their support and encouragement.

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A. I. ANDREWS.

March 11, 1935.
University of Illinois, Urbana

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ENAMELS

CHAPTER 1

The History of Enameling

If we seek the origin of enameling, we must go far back into history, for the art of enameling small articles, such as jewelry, began in the centuries long before the birth of Christ. In tracing the beginnings of this now common art we always become confused, for the footprints of the pioneers have long been trodden over, and much of the work has been destroyed, damaged, or is in such a condition that it cannot be identified. There were enamelers in early times, however, for they have left traces which cannot be denied, even by the most conservative person. Just who the first was, whence he came, or where he worked probably never will be known. We know where enamels were found and we have good reason to believe that they were made near that locality, but the chances that they were transported are great, and we cannot be sure. We know that these enamels were not made after such and such a date in history, but we do not know how long prior to that date enameling actually originated.

It is likely that the Egyptians were the first to make enamels, but it is not probable that, for many centuries, they got beyond the threshold of enameling on metals. In their jewelry they used glass in the form of a cloisonné, and from the time of the beginning of the Christian era there are many examples of Egyptian enamels on jewelry, which treasures can be seen now in the large museums throughout the world. Blue and white were the only vitreous colors possessed by the Egyptians for a long period of time, the blue itself being faded because of the disintegration of the enamel surface. It now appears as a light dust blue instead of the dark blue, which is still evident when the weathered surface is removed by scraping.

In early history enamel was called "electron," which leads to considerable confusion in reviewing the literature of enameling, for electron was used also to designate certain alloys and amber. If the word electron actually refers to enamels in Homer's writings, then we have definite evidence that the art of enameling antedates the siege of Troy. Regardless of this evidence, however, there are examples of enamels in most large museums, which date back to the fourth century before Christ. These generally take the form of small petals of

flowers enameled on jewelry, some of which are at the present time in fairly good condition. They were undoubtedly executed by goldsmiths, the enameling itself being crude compared with the artistic effect of the metal work. Many of these enamels have completely disintegrated, while others have become loosened from the metal and have been lost.

In the early days of enameling the goldsmith and the glass blower undoubtedly worked together to develop the many variations accomplished. The literature is vague, however, and we only know that the art of enameling was practiced, but by whom or just how it was done we have but faint knowledge.

The art of enameling began to take definite form in the early part of the Christian era, this being called the Byzantine period, as the greatest development seems to have centered around Byzantium. The enamels developed in this period are classified into two groups, *cloisonné* and *champlevé*, depending on their method of fabrication.

To understand the development of the art of enameling, it is necessary to know how these different types of enamels were made.

The goldsmith was probably responsible for the first method, which is known as *cloisonné*. Being accustomed to the process of soldering small bits of metal together and making elaborate designs with delicate gold and silver wire, he naturally applied his craft to the problem of enameling. Fine wire was first soldered so as to form a border around the designs he wished to enamel. The next step in the process was that of filling the areas to be enameled with the powdered materials, either in the dry condition or as a soft paste. They were pressed firmly into place, smoothed off, and then placed in a furnace where the heat melted the enamel to a smooth surface of glass. Often it was necessary to make several applications before the correct thickness was obtained. This piece of crude enamel was then ground down until the gold wire appeared as a boundary around each design or different color. This gave a pleasing appearance and when finally polished was a very artistic piece of work, samples of which are common, yet highly prized.

When the coppersmith was faced with the problem of enameling, he had his own way of doing things which he applied to the work in hand. Instead of working with delicate bits of metal, he was accustomed to work with comparatively heavy stock, so the methods of the goldsmith did not appeal to him. He found it much more convenient to carve and gouge out than he did to build up his bronze, copper, and other heavy metals. He applied his enamels as the gold-

smith did and fired them in a similar manner. When the enamel was opaque, it was not particularly necessary that the metal be smooth, but when transparent or translucent enamels were used every irregularity showed, a fact which was sometimes utilized to obtain special effects. By gouging the metal to various thicknesses, it was possible to obtain attractive effects, some of which are very artistic. *Champlevé*, like *cloisonné*, is very common, and at later dates we find them interchanged from one metal to another.

Archaeologists claim to have discovered at Mont Beauvray, the home of the ancient Biberate, not only the enamel, but also the kiln used by the enamer. It is generally agreed that the first real progress in the art of enameling took place at Byzantium, now the location of what is Istanbul, which was so closely associated with Persia that the Persian influence is evident in the design of these enamels. These Byzantine enamels seem to have been the stimulus for the spread of enameling throughout Europe, during the period following the sixth century A. D. Enameling, however, did not reach Britain or Ireland until a very late date, the only early enamels in Britain being those which were introduced during the Roman Conquest, after which enameling in that part of the world died out for many centuries.

The influence of Byzantine enamels was widespread throughout the continent. *Theophanie*, a Byzantine princess who married Otto II, took with her to western Europe a group of her enamellers from the East. This group spread the knowledge of the craft very rapidly, and after the sixth century, we find the growth of enameling in every direction. From the latter part of the ninth to the eleventh century, these enamels flourished exceedingly, and our museums have an abundance of the work of this period. In the eleventh century, Byzantine enamellers were taken to Italy by the Abbot of Monte Cassino, and, although there had been enameling in Italy, this spread the influence of the art.

The art traveled as far as Milan, and in the twelfth century it was well established in Germany. Although there are many examples of enamels in our museums, dating prior to the sixth century, which are traceable to Gaul, Rome, and Britain, the greatest progress was made, at a later period, in Cologne, Treves, Maestricht, and Verdun, a group of towns close together. Limoges, Paris, and Toulouse also became famous, and in the Middle Ages, Limoges achieved a great reputation. This reputation was acquired because of the high quality of the work developed.

The history of enameling in the East is even more difficult to

follow than it is in Europe. There is, however, little likelihood that enameling was practiced in China prior to the Mongolian Invasion in the thirteenth century. The earliest specimens are crude and are believed to have been made in the middle of the fourteenth century. In the sixteenth century, enameling found its way from China to Japan, where it was later developed to a considerable extent. India likewise received its impetus to enameling from the West at about the same time. There is some evidence of enamels having been made in Siberia between the third and the sixth centuries, and some investigators believe that enameling actually first originated in Russia, and was carried from there to Egypt and then to Europe.

Having reviewed briefly the history of the art of enameling to the close of the fifteenth century, we are now ready to view the new era of enameling, when the art became the enameling industry. Prior to this period, enamel had been used in the form of insets and jewels, similar to the use of precious stones and gems. The new era was marked by the beginning of the practice of applying enamel in the form of a paint, and then melting it onto the metal. It is likely that painted-on enamels originated in Venice, but exact information concerning the origin is not available and probably never will be. Angelo Broviero, a glass worker, first discovered the use of enamel on glass, a process which he practiced for many years in Murano. The painting of the enamel powder onto metal as a means of application met with many difficulties, such as poor adherence and covering power. As the process was very useful, it was, however, rapidly perfected and much of the difficulty was overcome by using enamel on both the face and the back of the metal. This prevented the strains from causing the enamel to chip off and also permitted the use of thicker coats and more applications. The method used in France was that of applying a dark colored enamel to the back of the metal, and a white to the surface it was desired to enamel. Over this white surface pictures were applied in darker colors, similar in design to woodcuts. Later many colors were employed, and the enamels began to show a great variation. Flesh color and pink were desired but most difficult to attain. The "Miniature Style" developed out of this art in the middle of the sixteenth century, first being used by Jean Tontin, a goldsmith at Chateaudun, but later becoming famous through the great skill of the miniature painter, Jean Petitot (1607-1690).

These painted-on enamels mark the transition between the use of enamels for small pieces only, and the development of the industry, which is serving mankind so successfully.

Enamels passed through the stages in which they were applied only to gold, then silver, bronze, and finally copper. The application to iron was the next step and it was on this metal that enameling found its most important use. The development of enameling had taken place very slowly, but the period when iron was first enameled was one of great technical advance. The metallurgy of iron and steel was progressing rapidly, chemistry was making great strides, and the world, both industrially and socially, was undergoing great changes. This new age of iron, steam, coal, machinery, and science stimulated enameling and it progressed with the others.

The history of the development of iron enameling is exceedingly interesting, as it is so closely related to the advances of the other industries. The first iron enameling recorded is that on cast iron in the early part of the nineteenth century. The cast iron shapes were thoroughly cleaned and heated to redness in a muffle furnace, whereupon the hot ware was removed from the furnace and the enamel was dusted (shaken) upon the metal as a fine, dry powder. As the powder struck the hot iron, it softened and adhered to it. After applying the enamel, the piece was returned to the furnace and the enamel melted down to a smooth glass, and then removed from the furnace and allowed to cool. This method involved a ground coat or first coat of different composition from the cover or finish coat of enamel. In fact, it was usually necessary to make a number of applications of enamel, heating before each separate coat, to obtain a layer thick enough to give the desired effect. The enamel had to be easily fusible, and the operations were very expensive. The muffle furnaces were very inefficient, and many pieces were damaged because of the fuel gases, which turned the enamels black or caused them to blister. Although many difficulties were encountered, this method has, with many modifications and improvements, survived time, and is at the present being used for enameling great quantities of our modern ware. It is particularly suitable to the enameling of large cast iron pieces such as sanitary ware and barber chairs.

Enamel was first applied commercially to sheet iron and steel in Austria and Germany in the period closely following 1850. Experiments on sheet steel enameling date back to 1840, the development period including such names as Bartelmus, Gnüchtel, Thale, Ulrich, Kerkmann, Gebler, and finally in later years, after 1865, Haardt, Wuppermann, Amberg, and Baumann. This Austrian and German enamel was first applied only on the interior of the sheet steel vessels to be enameled. In firing the ware, it was introduced in a cooler

part of the furnace; then by means of tongs it was gradually moved to the hotter areas. When the firing was finished, the pieces were removed from the furnace, cooled, and the exteriors were painted with an ordinary black paint.

Moritz Vogelsang, of Vieweg in Braunschweig, published the first manual on enameling in 1851. In this paper he described the process and the materials used. Although now obsolete, it shows that the enameling industry was attracting the best chemists of the time and that it was being developed according to the best knowledge of the day.

One of the most important obstacles to rapid advance in enameling in this period was the lack of good, pure, and cheap raw materials. The technology of iron was not developed and the many chemical industries furnishing the raw materials for the enamels were in the process of development.

With the discovery of the Le Blanc and the Solvay soda processes, by which cheap and good soda was put on the market, enameling received quite a boon. The development of the improved methods of manufacturing borax and the discovery of new deposits of raw materials aided the enameLER. In 1860, the scientific investigation of the Stassfurt deposits had a pronounced effect, since it also lowered the cost of many materials and made new ones available.

In early enameling, copper, smalt, and zaffers were the exclusive sources of coloring materials producing blue, but these materials varied so in composition that no uniformity in the color of the enamel could be attained. The Saxon Blue Color Works discovered a method of making cobalt oxide from the silicate, a product which was very pure and could be used to give a uniform blue color. Other color oxides and materials were slowly added to the palette of the enameLER and the use of tin oxide as a white opacifier was introduced.

Probably one of the greatest boons to the enameling industry was the discovery of the use of clay to keep the powdered enamel in suspension in water and make it adhere to the metal before firing. This suspension of enamel and clay in water was called a slip, and was painted or poured on the metal, dried, and then fired in a furnace. At a much later date, the spray gun was developed, greatly facilitating the uniform application, especially on large pieces of ware.

The use of enamel slips became known as the wet process, and the powdering-on as the dry process. Both are in use at the present time, the dry process being employed almost exclusively for cast iron, while the wet process is used both for cast iron and sheet iron or steel ware.

As the new methods of making iron, the Bessemer, Thomas, Gilchrist, and Siemens-Martin processes were developed, new problems confronted the enameler. One of his raw materials, the iron on which he fired his enamel, was being changed and his former enamel compositions would no longer fit the new metal. The properties of the new iron were different, and a general readjustment was necessary. To correct the new difficulties, much experimentation was carried on by engineers, chemists, ceramists, and enameleurs all over the world. The methods of shaping the new metal were soon developed but it remained for the German and Austrian enameleurs first to enamel the new iron successfully. It was necessary to develop new formulae and use entirely different enamels for the new processes. In this work materials, such as lead and other poisonous oxides, were largely eliminated, and the new industry flourished. Science all over the world began to aid the enameler and the old empirical methods were gradually displaced. Up to the present era, however, some of the plants have held to the old methods, but advances have been rapid and the importance of formulae is gradually being replaced by a better appreciation and knowledge of scientific principles.

The greatest advances, however, have taken place since the beginning of the twentieth century, when enameling progressed rapidly in America. The first few years of this century showed an increase from a few small plants to thirty-five or forty in the United States and Canada. The plants grew rapidly in size and number, some employing as many as one thousand persons in 1910. In 1925 the product output amounted to six hundred and seventy-five million dollars. Such an increase naturally attracted not only capital but also the best ceramists, chemists, and engineers of the country. The chemical industry began to appreciate the market the enameler offered, and catered to his requirements. The steel industry made great strides in the development of better enameling irons. From the last years of the World War until 1930, the industry boomed.

The old type of agate or granite enamel no longer met the demand, and new developments in formulae and processes were made. The technique of sand blasting, cleaning, pickling, application, and firing was greatly improved. The continuous enameling furnace, automatic control, continuous conveyors, and mass production resulted from the increased demand. The amount of scrap and defective ware was greatly reduced, although the specifications for quality were made more severe.

Enamel frit manufacturing companies were organized, furnishing

uniform frit to many enamelers who had laboriously and inefficiently tried to make their own. The old rule-of-thumb period was over, and those who tried to stay with their code of secret formulae soon discovered that they were being left behind. The interchange of ideas became imperative, and the literature showed the effect. The American Ceramic Society encouraged the enameLER to publish his findings and soon many publications on vitreous enamels were appearing in the literature. At the present time there are several trade papers devoted exclusively to vitreous enameling. The result has been greater co-operation and better conditions throughout the industry. The publications of the government bureaus and the universities have added a great deal to our knowledge. The Porcelain Enamel Institute has made great strides in promoting the use of enamels and in organizing the enamel industry.

Probably one of the most important changes taking place in the industry is the appreciation of the exact knowledge of chemistry, physics, and engineering. The appreciation of research and development work in the years since the World War has raised the enameLER from the position of the rule-of-thumb man to one who knows his business. The industry today is not dormant, but is actively growing and improving through all the phases of science, industry, and economics. It is one of the important industries contributing to modern civilization and the present mode of living. During 1933 and 1934 it has again demonstrated its worth by organizing to a rapid recovery from the world's worst depression. The enameling industry now looks forward to even greater expansion.

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CHAPTER 2

Raw Materials for Enamels

A familiarity with the physical and the chemical properties, the impurities, and the sources of the raw materials used in enamels, is one of the enamel maker's greatest assets. These raw materials are drawn from all parts of the world and include minerals, rocks, and clays, as well as a great variety of chemicals manufactured, either as products or by-products of the chemical industries.

In the making of enamels it is generally necessary to use high grade materials, the physical condition often being equally as important as the chemical composition. In an efficient control of the raw materials for enamels, it is, therefore, often necessary not only to guard the purity, but also the fineness, mineral composition, method of manufacture, grain shape, distribution of fines, and many other conditions.

These different materials enter the enamel composition either in the raw batch or in the mill additions. The raw batch constitutes the greater bulk of the enamel, its constituents being melted to a glass and then quenched to a frit in water. To this frit the mill additions are then made and the whole mass is ground in ball mills to the proper fineness. The mill additions, exclusive of the water, seldom exceed fifteen per cent of the frit and in some cases, as in dry process cast iron enamels, may be entirely omitted. The mill additions consist of water, clay, opacifiers, gum, colors, and electrolytes, which are discussed in Chapter 9, under the title, Mill Additions.

The raw materials used in enamels may be divided into six different groups, namely, refractories, fluxes, opacifiers, colors, floating agents, and electrolytes.

The refractories include such materials as quartz, feldspar, and clay, which contribute to the acidic part of the melt and give body to the glass.

The fluxes include such materials as borax, soda ash, cryolite, and fluor spar, which are basic in character and react with the acidic refractories to form the glass. They tend to lower the fusion temperatures of the glasses but, if added in excess, they form slags.

The opacifiers are compounds added to the glass to give it the white opaque appearance so characteristic of vitreous enamels. Opacifiers are in general quite refractory, but the real opacifiers (tin oxide, antimony oxide, sodium antimonate, and zirconium oxide) are often

aided by accessory opacifiers, such as cryolite and fluorspar, which make the enamel much more fusible.

The color materials may be oxides, elements, salts, or frits, and may act either as refractories or fluxes. The color contributed to an enamel may be influenced by the enamel composition and the processing.

The floating agents are mill additions such as clay and gums which are used to suspend the enamel in water or in some other liquid. Many different varieties of clay are used, but a plastic clay quite free from impurities is required. Such gums as tragacanth and arabic are often used for enamels where brushing is desired. To deflocculate the clay and properly suspend the enamel, electrolytes are added. These are such compounds as borax, soda ash, magnesium sulphate, and magnesium carbonate, which, when added in very small amounts, aid the clay in keeping the enamel in suspension. They often form buffer solutions, and, thereby, control the hydrogen ion concentration of the slip. Some electrolytes, however, are specific in their action.

The following is a classification of the more common enamel materials:

CLASSIFICATION OF ENAMEL MATERIALS

<i>Electrolytes</i>	<i>Fluxes</i>	<i>Refractories</i>
Borax	Borax	Quartz
Soda ash	Soda ash	Feldspar
Magnesium carbonate	Soda nitre	Clay
Magnesium sulphate	Fluorspar	Rutile
	Cryolite	
<i>Colors</i>	Whiting	<i>Floating Agents</i>
Cobalt oxide	Barium carbonate	Clay
Copper oxide	Magnesium carbonate	Gum tragacanth
Iron oxide	Litharge	Gum arabic
Nickel oxide	Red lead	Ammonium alginate
	Zinc oxide	Bentonite
<i>Opacifiers</i>		
Tin oxide		
Antimony oxide		
Zirconium oxide		
Sodium antimonate		

Since an adequate discussion of the raw materials entering enamel compositions would be very extensive, and might well be given in a book on that subject alone, no attempt will be made here to cover the subject. The information on raw materials is available in many places, but to give the enameler a ready reference to the fundamental characteristics of these materials, these data have been compiled in Table 1.

TABLE 1—(Continued). ENAMEL RAW MATERIAL

MATERIAL	FORMULA OF PRINCIPAL CONSTITUENT	COMMON IMPURITIES	COMMON LIMITATIONS %							COMMON AMOUNT % (seldom used)				
			SSG	SSC	DPG	DPC	WPG	WPC	SSG	SSC	DPG	DPC	WPG	WPC
Manganese dioxide	MnO ₂	SiO ₂ , Fe oxides	0-2	0-7C	0-5	0-7C	0-7C	1-5
Nickel oxide (gray)	NiO	As, Fe, S	0-3	0-7C	0-3	0-7C	0-7C	.5
Nickel oxide (black)	Ni ₂ O ₃	As, Fe, S	0-3	0-7C	0-3	0-7C	0-7C	.5
Nitre	KNO ₃	Na ₂ CO ₃ , Cl, SO ₄	0-5	0-5	0-5	0-5	0-5	3	3	3	5	3	5
Pearl ash	K ₂ CO ₃	Na ₂ CO ₃ , Cl, SO ₄	0-12	0-12	0-10	0-10	0-10	0-10
Potassium carbonate	K ₂ CO ₃	Na ₂ CO ₃ , Cl, SO ₄	0-12	0-12	0-10	0-10	0-10	0-10
Potassium nitrate	KNO ₃	Na ₂ CO ₃ , Cl, SO ₄	0-5	0-5	0-5	0-5	0-5
Pyrolusite	MnO ₂	SiO ₂ , Fe oxides	0-2	0-7C	0-5	0-7C	0-7C	1.5
Quartz	SiO ₂	Fe oxides	10-30	0-35	10-45	0-35	5-25	7-25	22	20	25
Red lead	PbO ₂	Pb oxides, BaSO ₄ , Pb, Fe ₂ O ₃ , PbS	0-12	0-25	0-12	0-38
Rutile	TiO ₂	Fe oxides, SiO ₂	0-6	0-8	0-8	0-8
Saltpetre (Chile)	NaNO ₃	Cl, SO ₄ , Fe oxides	0-5	0-5	0-5	0-7	0-5	0-7	3	3	3	5	5
Sand	SiO ₂	Fe oxides	10-30	0-35	10-45	0-35	5-25	10-25	22	20	25	11
Silica	SiO ₂	Fe oxides	10-30	0-35	10-45	0-35	5-25	10-25	22	20	25	11
Silicate of soda	Na ₂ SiO ₃ (Variable)	Na ₂ CO ₃ , Cl, SO ₄ , Na ₂ O	0-20	0-20	0-20	0-20	0-20
Soda ash	Na ₂ CO ₃	Cl, SO ₄ , K, Ca	0-12	0-12	0-5	0-12	0-8	0-8	7	4	3
Sodium fluoride	NaF	CaF ₂ , Na ₂ O	0-10
Sodium meta antimonate	NaSbO ₄	Sb ₂ O ₃ , Na ₂ O, Cl, SO ₄	0-18	0-13	0-5	0-5	(8)	10	2
Soda nitre	NaNO ₃	Cl, SO ₄ , Fe oxides	0-5	0-5	0-5	0-7	0-5	0-7	3	3	3	5	5
Sodium silicofluoride	Na ₂ SiF ₆	SiO ₂	0-10	0-10	0-10	0-10
Sodium silicate	Na ₂ SiO ₃ (Variable)	Na ₂ O, SiO ₂ , Cl, SO ₄	0-20	0-20	0-20	0-20
Spinel	ZnO, Al ₂ O ₃	ZnO, Al ₂ O ₃ , Na ₂ O, B ₂ O ₃	Seldom used.
Tin oxide	SnO ₂	Sn, SnO	0-7M	0-12	0-7M	M5	8	5
Titanium oxide	TiO ₂	TiO, SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃	0-6	0-7	0-7	0-7	0-5	(5)	(5)
Whiting	CaCO ₃	MgCO ₃ , clay, SiO ₂ , Cl, SO ₄	0-7	0-5	0-6	0-6	(3)	2
White lead	2PbCO ₃ ·Pb(OH) ₂	Pb, BaSO ₄ , PbSO ₄ , CaCO ₃	Seldom used.
Zinc oxide	ZnO ₂	Zn, PbS, Cd, Fe oxides	0-6	0-12	0-12	(5)	8	5
Zirconium oxide	ZrO ₂	SiO ₂ , Na ₂ O, Al ₂ O ₃ , P ₂ O ₅ , TiO ₂	0-10	0-7M	0-7M	5M	5M	5M

M=Mill addition
C=Color material

SSG=Sheet steel ground
SSC=Sheet steel cover

DPG=Dry process ground
DPC=Dry process cover

WPG=Wet process ground
WPC=Wet process cover

This table includes exact data concerning each of the enamel raw materials and will answer most of the questions with which the enameler will be confronted. A familiarity with these tables will greatly facilitate the compounding of enamels.

The functions of the raw materials, both in the frit and in the mill additions, will be discussed in detail with reference to the particular enamel compositions, throughout the text.

Dehydrated Borax. Dehydrated borax ($\text{Na}_2\text{B}_4\text{O}_7$) has recently become available in quantities sufficient for use in enamel manufacture. The principal advantages of dehydrated borax are the reduction in the amount of material which must be handled, stored, and shipped, and the fuel saving realized in smelting. The heat used to dehydrate the borax in the ordinary batch is an appreciable factor which is saved when dehydrated borax is used. If adopted and substituted in present enamels, the appearances of the batch compositions will be changed since the borax content will be reduced to one-half of that used as the ordinary decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). To convert the ordinary hydrated borax to the dehydrated borax multiply by 52.8 and divide by 100.

The calculation factors for changing the dehydrated borax to melted composition are: $\text{Na}_2\text{O} = 0.308$, $\text{B}_2\text{O}_3 = 0.692$. The molecular weight is 201.3, the density is 2.36, and the weight in pounds per cubic foot is 63 to 82. It is white in color, soluble in water, and has a melting point of 741°C . Results of tests in commercial enamel smelters indicate that the dehydrated borax functions the same as the hydrated borax with much less frothing and boiling.

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CHAPTER 3

Fundamental Considerations

The chemistry and physics of high temperature phenomena are not as well known as those at normal temperatures, but the fundamental laws of these sciences apply, regardless of the temperature. Reactions at elevated temperatures are much accelerated because of the increased molecular activity, and in some cases these reactions are reversed or caused to proceed in different directions. Compounds which are stable at ordinary temperatures may become unstable and decompose at elevated temperatures. Other compounds may become more stable, some will melt, some boil, some sublime; the changes being from solid to liquid to vapor.

All materials have vapor pressures, some so small that they cannot be measured and others so high that they change from solid or liquid to vapors quite rapidly. If it were not for the atmospheric pressure, many more of our materials would exist only in the gaseous state. Boiling is the phenomenon which takes place when the vapor pressure of the liquid just exceeds the atmospheric pressure. The vapor pressure of a material usually increases with an increase in temperature, therefore by increasing the temperature of a liquid, the boiling point is approached. The vapor pressure of water, for example, increases as the temperature is increased to 100 degrees Centigrade (212 degrees Fahrenheit) where it equals the atmospheric pressure at sea level. If the atmospheric pressure is reduced, water will boil at lower temperatures than this, since the vapor pressure of the water will exceed the reduced atmospheric pressure at a much lower temperature, a condition which is often used in drying materials that decompose at a temperature of 100 degrees Centigrade or below.

Although water at low temperatures does not have a vapor pressure equal to atmospheric pressure, it does have a measurable vapor pressure, which causes the water to evaporate until it either develops a pressure over it equal to its vapor pressure, or until the water completely evaporates. Solid water (ice) has a vapor pressure and in the open air it evaporates, even though it is kept at a temperature below freezing. This is evidenced by the disappearance of snow in the winter, when the temperature remains below freezing.

What is true of water in this respect is also true of other materials, but the values of the vapor pressures vary. Some materials sublime (arsenic oxide, for example). Sublimation is possible in the atmos-

phere, when the vapor pressure exceeds the atmospheric pressure below the melting temperature of the material. By reduction of the atmospheric pressure many materials, which would ordinarily be melted under standard atmospheric conditions, can be sublimed.

Although considerations of vapor pressures are not common in the enameling industry, they are important; for many of the constituents of an enamel have appreciable vapor pressures at the smelting and firing temperatures. In some cases, where especially fine enamels of high opacity are desired, the melts are made in covered crucibles. The author has verified this by experiments with certain jewelry enamels, it being impossible to get as good opacity in high fluorine melts exposed to the atmosphere as those made in closed crucibles. In glazing, this is common knowledge, especially in the firing of lead-bearing glazes and in the firing of certain colors. In firing lead glazes the ware is placed in closed saggars (clay boxes), which are coated inside with a slip containing a high percentage of lead oxide. This lead oxide slip saturates the atmosphere within the sagger with lead vapors, which reduce the vaporization of the lead from the glaze. If this is not done, the glazes are dull, lacking the gloss which should be contributed to them by their lead content. The vaporization of the lead in the glaze is reduced, at a given temperature, by putting it under an atmospheric pressure of lead-bearing gases. In the firing of colored glazes it is a well-known fact that many of the color oxides, such as copper and chromium oxides, vaporize during the firing and may contaminate adjacent glazed ware with color.

Compounds and elements generally become more active as they change from solids to liquids to vapors. Solids do not commonly react chemically with each other, except at very slow rates. The constituents of an enamel batch are very inert until heated to a temperature at which at least one of them melts, and forms a liquid phase.

As soon as the melt forms, the reaction begins. If one wishes to promote a reaction between two solid materials which are very inert, they can often be caused to react readily by melting. Mobile melts in general are subject to much more rapid reactions than viscous melts, as evidenced by the ease of crystallization from the former and the difficulty of crystallization from the latter. In the fluid melts the molecules are freer to move about, and a combination is much more likely, than in viscous melts. Any enameler is familiar with the ease of getting a good uniform frit when the melt is mobile, and with the difficulties encountered when the melt is viscous. Gases dissolved in the melt make it more fluid, a fact which must be considered in smelting.

If a batch is smelted too rapidly, the gases are evolved from the batch before they have accomplished their function of aiding the chemical reaction.

Solubilities usually become greater as the temperature increases. Solubility is a very important consideration in enamels, for an enamel is essentially a super-cooled solution. The first material melting during the smelting process proceeds to take the other constituents into solution in it. Many of the materials used in enamels have melting points well above the smelting temperature of any enamels. These materials are dissolved by the more fusible constituents. The solution is often accompanied by decomposition with the evolution of gases, which are partially, at least, dissolved in the melt. The evolution of these gases agitates the melt and, therefore, brings about a better condition for further solution and reaction of the various constituents.

Many materials go through inversions from one crystalline form to another at definite temperatures without any change in chemical composition. Quartz, one of the most common enamel materials, undergoes many such changes, as indicated by the diagram, Figure 1. Some of these inversions, such as that from low quartz to high quartz (573°C) are very rapid, while others are very slow and sluggish, such as the inversion from high quartz to upper high tridymite (870°C). It is possible to have unstable forms existing for long periods of time, but a stable form at a particular temperature never inverts to an unstable form. Fluxes aid these inversions, since they furnish a liquid phase, through which solution and crystallization can take place. If an unstable form is soluble in the flux or melt, it will dissolve and crystallize out in a more stable form. If the unstable form is much more soluble in the flux than the stable form, the inversion is very much accelerated. In enamels, many fluxes are present and the solution of the quartz, tridymite, cristobalite, or vitreous silica is practically complete. It is claimed that vitreous silica is in general much more soluble in melts than the crystalline modifications of silica. At temperatures of an enamel melt, this vitreous silica is an unstable form, therefore its higher solubility is to be expected. Fused silica (silica glass) is becoming more common on the market, but is yet relatively expensive. The unstable form of a material, at a given temperature, always has a higher vapor pressure, than the stable form, which is another aid to the inversion through the vapor phase.

At high temperatures all the conditions of the solid, liquid, and gaseous phases, such as solutions, colloids, and suspensoids in general, are possible. There may be solutions of gases in solids or liquids, of

liquids in solids, and of solids in liquids. Immiscible molten liquids, suspensoids of solids in molten magmas, and solid solutions are encountered.

The colloids are similar to those forming at low temperatures and are, therefore, subject to the effects of electrolytes. The dispersion of

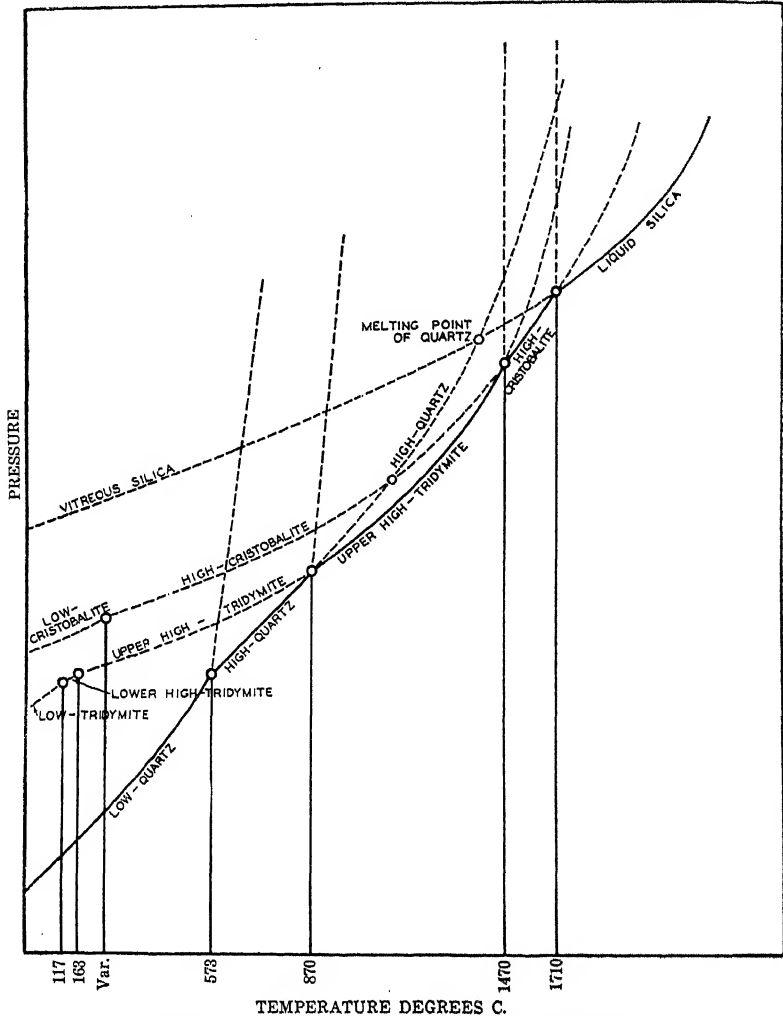


FIGURE 1. Stability Relations of the Silica Minerals.

the opacifier in some glasses is very good, probably caused at least in part by the charge on the particles. In most glasses the opacifiers tend to aggregate and in extreme cases two liquids are formed. In some

enamels the fluorine compounds act to disperse the opacifier, as is the case of tin oxide and calcium fluoride in certain dry process cast iron enamels. If the fluorspar is left out of the composition, the tin oxide tends to aggregate, but, if the fluorspar is present, the tin oxide is uniformly dispersed and a good quality of opacity is obtained.

Immiscible liquids are not uncommon in vitreous enamels. Sulphate melts do not mix with enamel melts but float on the surface of the molten enamel. An emulsion does not form and a separation is not difficult, since the sulphate melt is much more mobile and has a lower specific gravity than the enamel melt. In pouring the enamel, the sulphate melt flows off first and, if quenched in water, a violent explosion results, caused by the avidity of these anhydrous sulphates for water and the heat of reaction forming steam. Instances have been known where sulphates have been accidentally incorporated in enamel batches and serious explosions occurred. Any sulphur gases in the atmosphere over an enamel melt react with the melt to form alkali or alkali earth sulphates. The author has made melts in atmospheres with high percentages of sulphur and has found an appreciable amount of molten sulphates in the resulting enamel.

Some opacifiers, such as antimony oxide, are very refractory and, when they do not dissolve in the enamel melt, they are present as finely divided solid particles suspended in the molten enamel. Here we have a colloid and on solidification of the enamel the colloidal condition remains, giving, because of the multiple refraction of light, an opaque enamel.

Enamels are to be classed, in general, as solutions, whether they are solids or liquids. An enamel is essentially a super-cooled solution, holding certain materials in suspension.

It is interesting and instructive to note how close the reactions of different materials at high temperatures compare with the reactions at low temperatures. Many salts and some bases and acids preserve their identity and characteristic chemical properties when heated to smelting temperatures, even though dehydration may occur and certain gases be driven off. The periodic arrangement of the elements is just as useful at high temperatures as it is at low temperatures. It is interesting that the elements, cobalt and nickel, which give to a sheet iron ground coat its great adherence to iron, occur together with iron in the periodic table. Potassium and sodium, which are almost interchangeable in some enamels, occur together. Aluminum occurs between the bases and silicon, the same position as it holds in enamels. Magnesium, calcium, strontium, and barium occur in the same group near

sodium and potassium, and they react similarly in an enamel. Tin, antimony, and zirconium are closely associated in the table, and in enamels they are again grouped together as opacifiers. In this way it is possible to point out many characteristics which make a familiarity with the periodic table a great aid to the enamel chemist. Although it is recognized that there are some irregularities in the periodic table, it is recommended that it be kept in mind as it gives a systematic background for thought.

Research at high temperatures is more difficult and requires better control and technique than at lower temperatures, but it can utilize similar methods and predictions from a knowledge of chemical reactions at normal temperatures. A great deal of work has already been done on high temperature reactions, but because of the difficulties encountered, the available information is far from being as complete as that for lower temperature chemistry.

To understand the discussion of this information, it is necessary to know the meanings of the terms used, and the methods of plotting the data and interpreting the diagrams. The relations of the phases of the materials are plotted, considering such variables as composition, temperature, and pressure. Most of the systems to be dealt with in enamels involve only composition and temperature, the other variables being neglected, since their effects are generally of relatively minor importance. The materials plotted are termed *components*. A system contains one component if its composition can always be expressed in terms of one component. The silica system is a one-component system, for the composition of any of its forms can be represented as silica (SiO_2). A two-component system is a system in which the composition of any part of the system can be represented in terms of the two components. Thus, the alumina-silica system, Figure 7, is a two-component system of alumina and silica, since any compounds formed, or any part of the system, can be represented in terms of alumina and silica. The system $\text{NH}_4\text{OH} - \text{HCl}$ is not a two-component system, since in the reaction of these two components, NH_4Cl and H_2O are formed, neither of which can be represented in terms of NH_4OH and HCl . These new compounds NH_4Cl and H_2O are not additive compounds of NH_4OH and HCl ; therefore they act as new components, making the system a four-component system. Three-component systems can be represented in terms of not less than three components, four-component systems in terms of not less than four components, and so on.

The components of a system may form additive compounds and exist as solids, liquids, or gases. These forms are called *phases*. A

phase may be defined as any portion of a system which is homogeneous throughout and mechanically separable from the other parts of the system.

The degree of freedom of a system is the number of variables (temperature, pressure, composition, etc.) which must be fixed to define a system. The degree of freedom can be determined by use of the Phase Rule which is mathematically stated as follows:

$$F = C - P + 2$$

where F = the degree of freedom, C = the number of components, and P = the number of phases.

The diagrams, in general, represent equilibrium conditions, that is, conditions attained if time is unlimited. In plant practice such conditions are not always reached, and sometimes the unstable condition is also plotted for convenience. A system is in equilibrium, under set conditions, when it undergoes no change with the passage of time; provided, also, that the system has the same properties when the same conditions are obtained by two different procedures. Water, for example, may be carefully cooled below the freezing point, but in this condition it is unstable and a slight disturbance will cause it to crystallize as ice. Water in this condition is not in equilibrium, because the same condition could not be obtained by heating ice to a temperature just below zero.

Since an enamel is essentially a glass, much of the information available from glass research is applicable to enamels. The physical chemistry of glass has been extensively studied, yet this work is far from complete and it will be years before a sound understanding of the relations between composition, properties, and processing will be attained. Much of the fundamental research has been carried out on so-called simple systems, those more complicated having thus far yielded only information of a more or less specific nature. A vitreous enamel in its simplest form is a complicated glass; since the ordinary three and four component glasses do not make good enamels. The study of the relations of the oxides to each other in simple systems, however, does throw considerable light on the chemistry and physics of all glasses and enamels.

EQUILIBRIUM DIAGRAMS

The use of equilibrium diagrams is a great aid to the interpretation of the data obtained in the chemistry and physics of high temperatures. The diagrams of one, two, and three component systems are very useful, but the systems of more components are increasingly difficult to plot.

The diagram of a one-component system has already been mentioned as shown in Figure 1, for silica. These systems are all relatively simple, as the chemical composition always remains the same, the phases being physical modifications such as solids, liquids, and gas. Many substances have a number of solid modifications, as is illustrated with silica. Each of these modifications has its own range of temperature and pressure conditions. Any phase may occur in equilibrium with any other phase which has a common boundary line on the diagram. If, for example, a solid phase has a common boundary line with a liquid phase, one can be converted directly into the other. If no common boundary line exists between two phases, however, then such a change cannot take place under equilibrium condition. For example, low quartz inverts into high quartz and vice versa, but low quartz cannot invert to cristobalite without first being converted into high quartz.

The two-component systems are usually plotted as composition and temperature diagrams. The horizontal axis is used for the composition and the vertical axis for the temperature. The diagrams shown in Figure 2 give the more common types of two-component systems.

Figure 2a shows a typical system, in which two components A and B mixed together melt at lower temperatures than the pure materials. The lowest melting mixture E is called the *eutectic*.¹ The areas are labeled in the diagrams to show the phases which are in equilibrium under the existing conditions.

If a melt of composition X is cooled, crystals of A come out of solution at the temperature P, and the composition of the melt follows the curve from P to E. When the temperature reaches R, the remaining melt has the composition E, which crystallizes as the eutectic.

Figure 2b shows a typical isomorphous system of two components A and B. These two components crystallize together in various combinations. The upper curve L is the liquidus curve, and the lower curve S is the solidus curve. On cooling a composition X, the melt cools to the liquidus curve, and then the solid of a composition on the solidus curve corresponding to the temperature where X meets the liquidus curve, solidifies out. As the temperature is further lowered, the composition of the melt moves to the left along the liquidus curve, and likewise the composition of the solid formed moves to the left along the solidus curve until it reaches the composition of X, when the whole mass has become solid.

¹ A eutectic is the lowest melting mixture of two or more materials. The eutectic temperature is the melting temperature of the eutectic mixture.

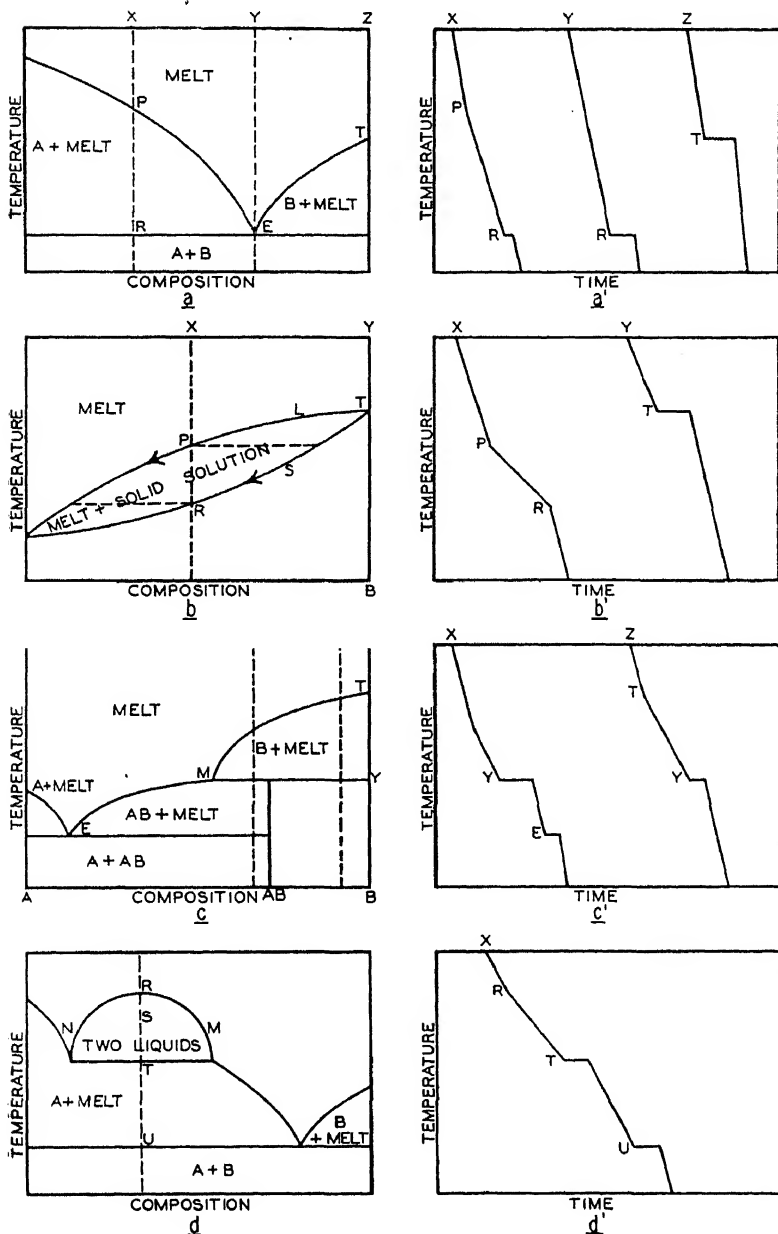


FIGURE 2. Two-Component, Composition-Temperature Equilibrium Diagrams and Typical Cooling Curves from which the Diagrams are Derived.

Figure 2c shows a condition of *incongruent melting*,² the compound AB decomposing into compound B and a melt M at the temperature Y. The cooling of a melt and the reformation of the compound AB is called *resorption*. This system has a eutectic between the compounds AB and A, but no eutectic between A and B, or B and AB.

Figure 2d shows the equilibrium relations of two immiscible liquids plotted on a two-component diagram. As melt X cools through temperature R, it breaks up into two immiscible liquids. At temperature S the two liquids have compositions M and N. At temperature T the liquids again become miscible, and crystals of A begin to form progressively until temperature U is reached. At temperature U the eutectic forms.

The time-temperature cooling curves for compositions X, Y, and Z in the diagrams a, b, c, and d of Figure 2, are as shown respectively in the corresponding diagrams a', b', c', and d'.

These latter diagrams show the rate of cooling, temperatures being plotted on the vertical axis and times on the horizontal axis. When a melt is cooled, it does so at a fairly constant rate until crystallization begins, which because of the exothermic effect slows the rate of cooling, as shown by the change in the slope of the curve. If the liquid crystallizes as a compound or a eutectic, the cooling may be completely arrested until solidification is complete. Wherever the change does not involve a gradual change in the composition of the melt, the temperature does not decrease further (the reaction being exothermic) until solidification is complete. Such conditions exist at the melting temperature of a compound, at the incongruent melting temperature, and at the eutectic temperature. In observing the curves a', b', c', and d' of Figure 2, it will be noted that at all temperatures where the melt reaches these conditions the time-rate cooling curve is completely arrested, and appears as a horizontal line until time sufficient for the change to take place has elapsed. Where cooling does not stop, but only decreases in rate, crystallization is taking place progressively while the melt cools through the liquid-solid area. Thus in curve X of Figure 2a', the melt X cools at a uniform rate to temperature P, where it encounters the liquidus curve. It then changes in rate as it passes through the solid-liquid area to temperature R, which is a eutectic temperature. At temperature R the cooling stops until the last trace of liquid disappears. The remainder of the cooling curve represents the cooling of the solid phases.

² Incongruent melting is the decomposition of a compound into a melt and a new compound at a definite temperature.

Other two-component systems are combinations of the four principles shown in Figure 2, and are amply illustrated in the following diagrams of equilibrium systems, which were selected as those of primary interest to the enameler.³ A complete description of each diagram is not given, as such would be a repetition and is unnecessary. The cuts for these diagrams were furnished by the American Ceramic Society.

Although the enameler has not extensively utilized such systems in the past, it is probable that they will play an important part in future research and development. It may well repay the reader to make a more extensive study of these physico-chemical principles than the limitations of this book permit.

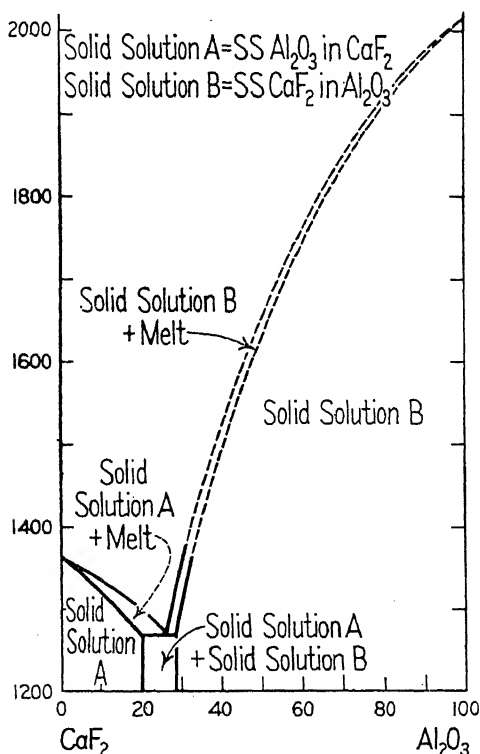


FIGURE 3. Equilibrium Diagram for the System; $\text{CaF}_2\text{-Al}_2\text{O}_3$, Pascal, Z. Elektrochem., 19, 610-13 (1913). J. Am. Ceram. Soc. 16, 455 (1933).

³ E. P. Hall and Herbert Insley, A Compilation of Phase Rule Diagrams of Interest to the Ceramist and Silicate Technologist. J. Am. Ceram. Soc. 16, 463 (1933).

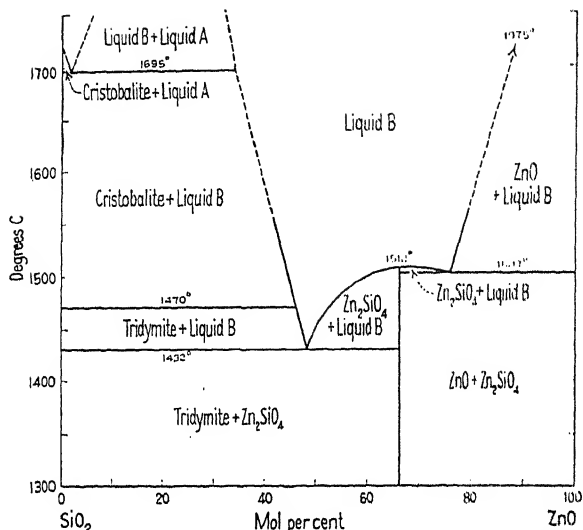


FIGURE 4. Equilibrium Diagram for the System; ZnO-SiO_2 , E. N. Bunting, Bur. Stand., Jour. Research, 4, 131-36, (1930), p. 134. See also E. N. Bunting, Jour. Amer. Ceram. Soc., 13 (1), 5-10 (1930), p. 8; Glastechnische Tabellen, p. 35, J. Am. Ceram. Soc. 16, 455 (1933).

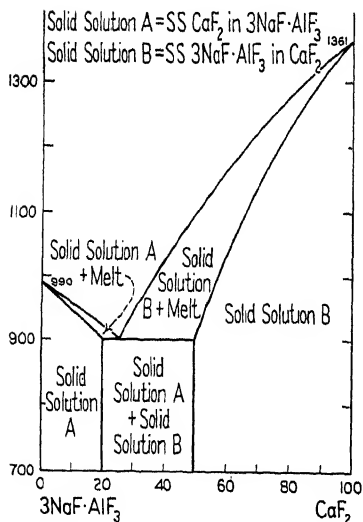


FIGURE 5. Equilibrium Diagram for the System; $3\text{NaF} \cdot \text{AlF}_3\text{-CaF}_2$, P. Pascal, Z. Elektrochem., 19, 610-13 (1913). J. Am. Ceram. Soc. 16, 455 (1933).

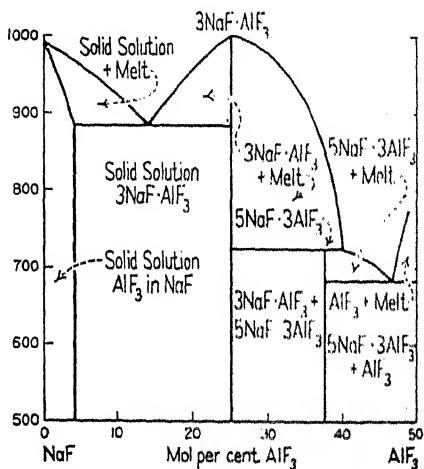


FIGURE 6. Equilibrium Diagram for the System; NaF-AlF_3 , Fedotieff and Iljinsky, Z. anorg. Chem., 80, 113-54 (1913); J. Am. Ceram. Soc. 16, 455 (1933).

FUNDAMENTAL CONSIDERATIONS

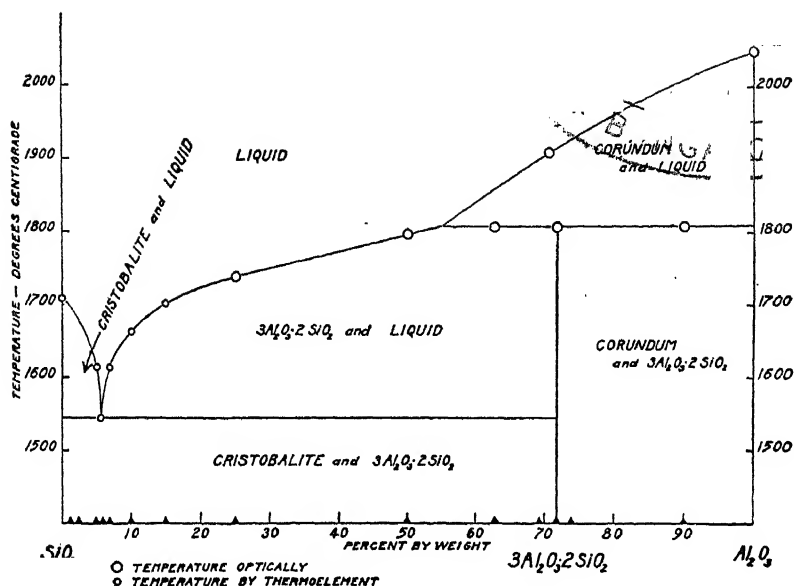


FIGURE 7. Equilibrium Diagram for the System; Al_2O_3 - SiO_2 , Bowen, N. L. and Greig, J. W., The System Al_2O_3 - SiO_2 ; J. Am. Ceram. Soc. 7, 238-54 (1924).

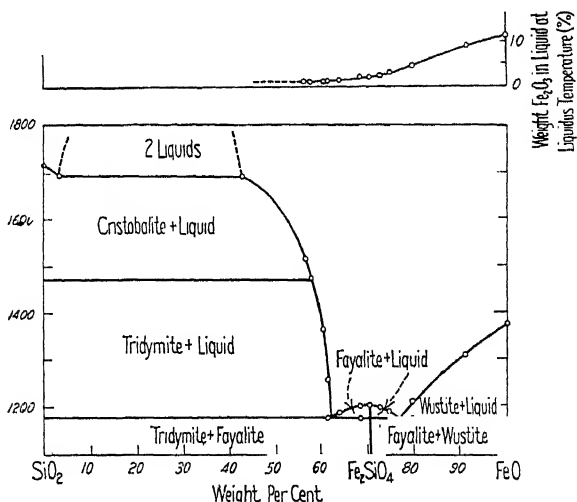


FIGURE 8. Equilibrium Diagram for the System; FeO - SiO_2 , N. L. Bowen and J. F. Schairer, Amer. Jour. Sci., 5th Ser., 24, 177-213 (1932), p. 200. J. Am. Ceram. Soc. 16, 455 (1933).

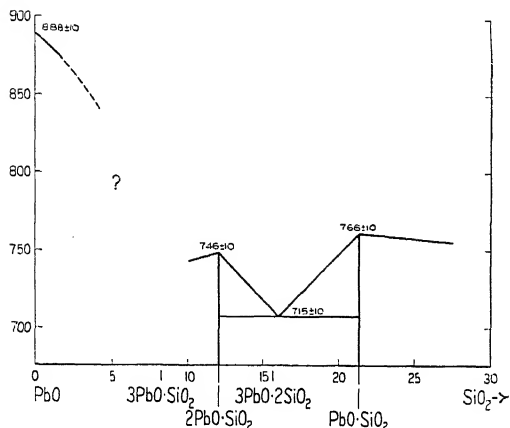


FIGURE 11. Equilibrium Diagram for the System; PbO-SiO_2 , H. C. Cooper, L. I. Shaw, and N. E. Loomis, *Amer. Jour. Sci.*, 4th Ser., 42, 461 (1909); J. B. Ferguson, *International Critical Tables*, 4, 83-97 (1928), p. 86. See also K. A. Krakau and N. A. Vakhrameev, *Trans. Opt. Inst. (Leningrad)*, 7 (79), 1-32 (1931); *Glastechnische Tabellen*, p. 36. *J. Am. Ceram. Soc.* 16, 455 (1933).

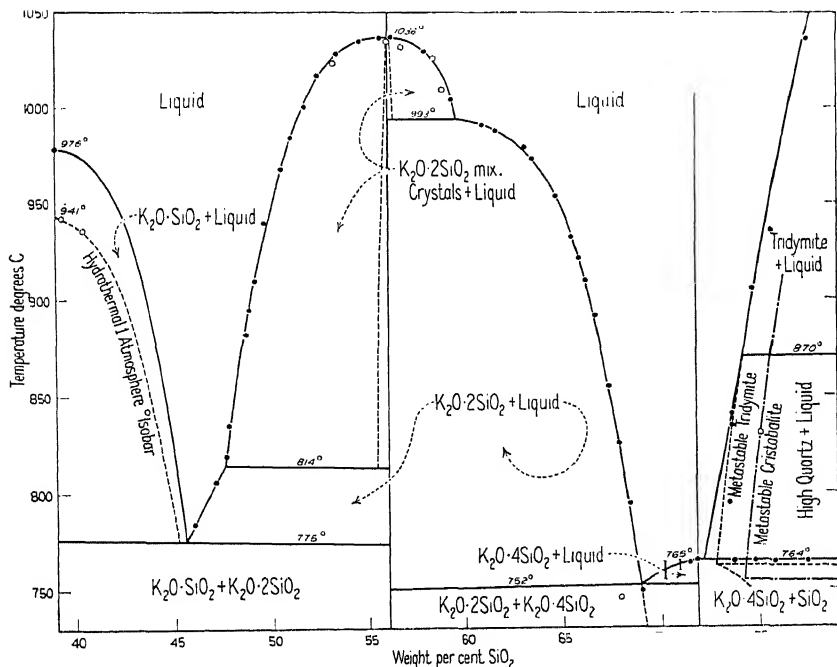


FIGURE 12. Equilibrium Diagram for the System; $\text{K}_2\text{O-SiO}_2$, F. C. Kracek, N. L. Bowen, and G. W. Morey, *Jour. Phys. Chem.* 33, 1857-79 (1929), p. 1872. See also *Glastechnische Tabellen*, p. 22. *Jour. Am. Ceram. Soc.* 16, 455 (1933).

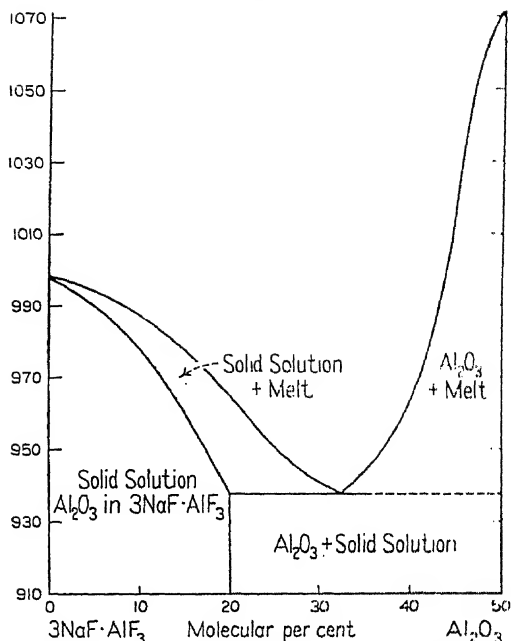


Figure 13. Equilibrium Diagram for the System; $3\text{NaF} \cdot \text{AlF}_3 - \text{Al}_2\text{O}_3$, Lorenz, Jabs, and Eitel, *Z. anorg. Chem.*, **83**, 39-50 (1913). *J. Am. Ceram. Soc.* **16**, 455 (1933).

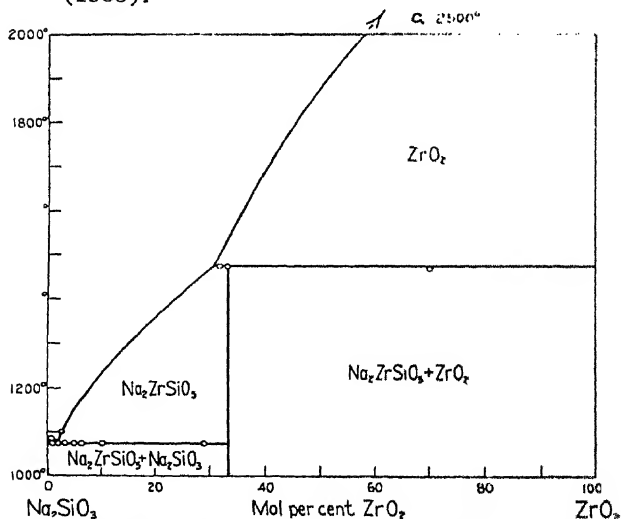


Figure 14. Equilibrium Diagram for the System; $\text{Na}_2\text{O} \cdot \text{SiO}_2 - \text{ZrO}_2$, J. D'Ans and J. Löffler, *Z. anorg. allgem. Chem.*, **191**, 1-35 (1930), p. 19. *J. Am. Ceram. Soc.* **16**, 455 (1933).

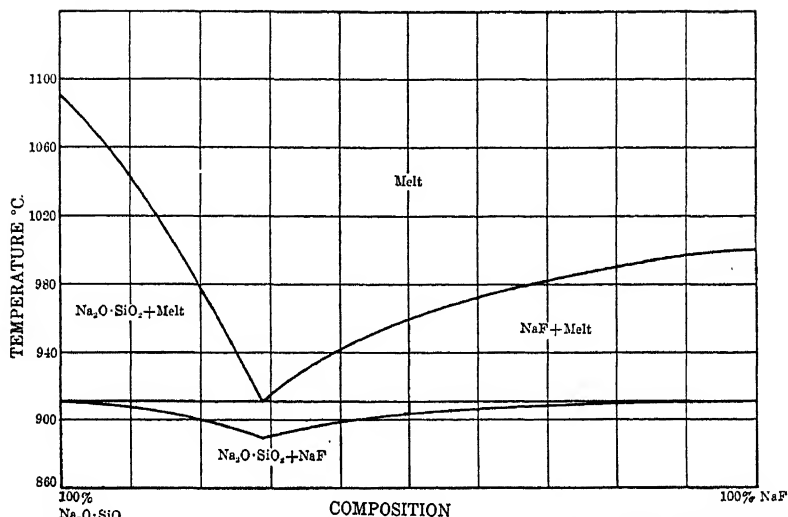


FIGURE 15. Equilibrium Diagram for the System; $\text{Na}_2\text{O} \cdot \text{SiO}_2$ - NaF , N. S. Booth and B. A. Starrs, Enamelist, Feb. (1932).

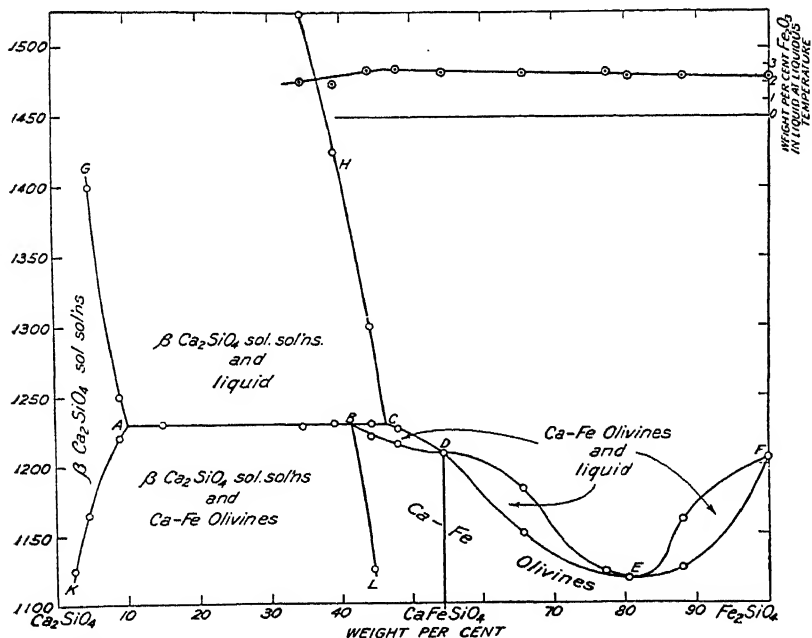


Figure 16. Equilibrium Diagram for the System; $2\text{CaO} \cdot \text{SiO}_2$ - $2\text{FeO} \cdot \text{SiO}_2$, N. L. Bowen, J. F. Schairer and E. Posnjak. A. J. of Sci. XXV, 273 (1933).

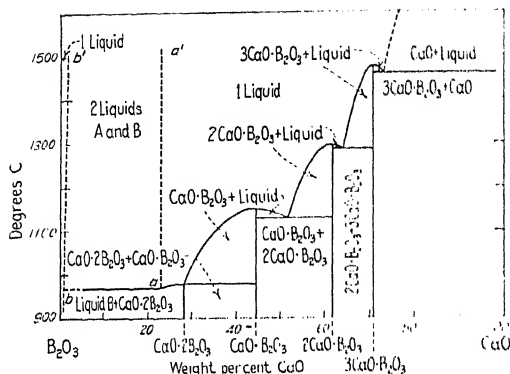


FIGURE 17. Equilibrium Diagram for the System; $\text{CaO-B}_2\text{O}_3$, E. T. Carlson, Bur. Stand., Jour. Research, 9, 825-32 (p. 830). J. Am. Ceram. Soc. 16, 455 (1933).

Compounds	$\text{CaO}(\text{Na}_2\text{O})/\text{SiO}_2$	Temp
SiO_2		100.0 1710 M
$\alpha\text{-CaO-SiO}_2$	48.3	51.7 1540 M
$\beta\text{-CaO-SiO}_2$	48.3	51.7 1180 I
$\text{Na}_2\text{O-SiO}_2$		50.8 49.2 1088 M
$\text{Na}_2\text{O-2SiO}_2$	34.1	65.9 874 M
$2\text{Na}_2\text{O-CaO-3SiO}_2$	15.5 34.4	50.0 1141 D
$\text{Na}_2\text{O-3CaO-6SiO}_2$	28.5 10.5	61.0 1047 D
$\text{Na}_2\text{O-2CaO-3SiO}_2$	51.5	55.5 234 M

M = Melting Point
D = Decomposition Point
I = Inversion Point

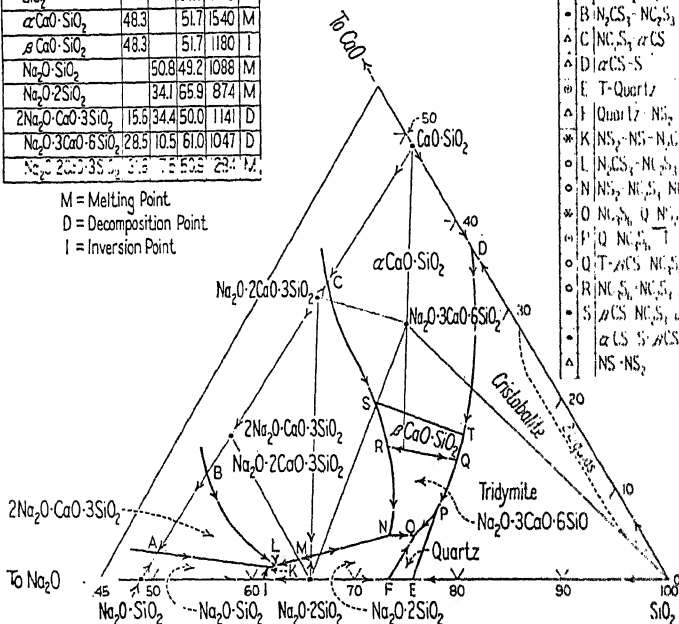


FIGURE 18. Equilibrium Diagram for the System; $\text{Na}_2\text{O} \cdot \text{SiO}_2\text{-CaO} \cdot \text{SiO}_2\text{-SiO}_2$, G. W. Morey and N. L. Bowen, Jour. Soc. Glass Tech., 9, 226-64, (1925), p. 233. See also Hewitt Wilson, p. 245; Glastechnische Tabellen, p. 43. J. Am. Ceram. Soc. 16, 455, (1933).

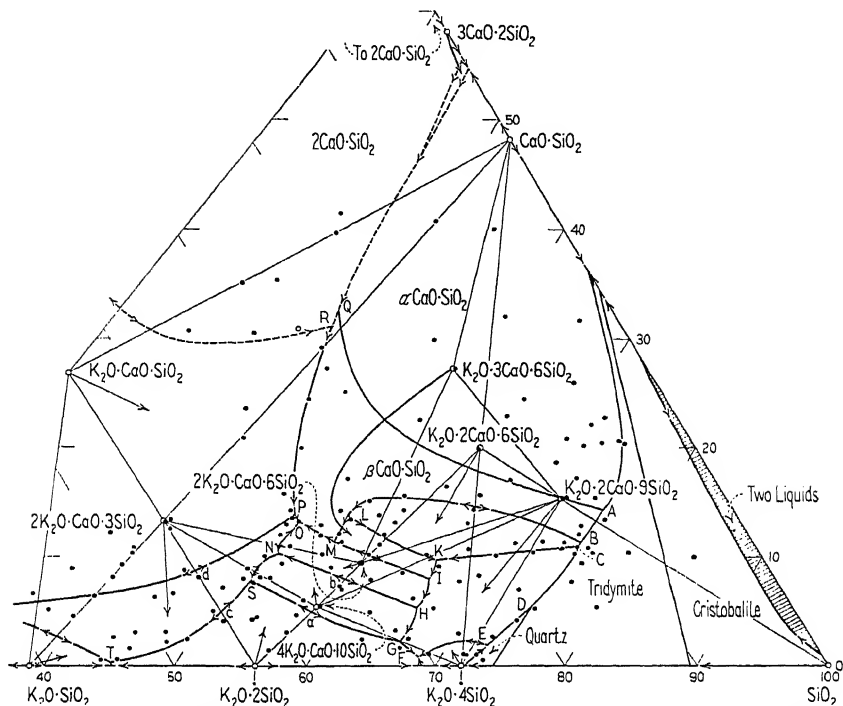


FIGURE 19. Equilibrium Diagram for the System; $K_2O \cdot SiO_2 - 3CaO \cdot 2SiO_2 - SiO_2$, G. W. Morey, F. C. Kracek, and N. L. Bowen, *Jour. Soc. Glass Tech.* 14 (54), 149-87 (1930), p. 158. See also *Glastechnische Tabellen*, p. 56, *J. Am. Ceram. Soc.* 16, 455 (1933).

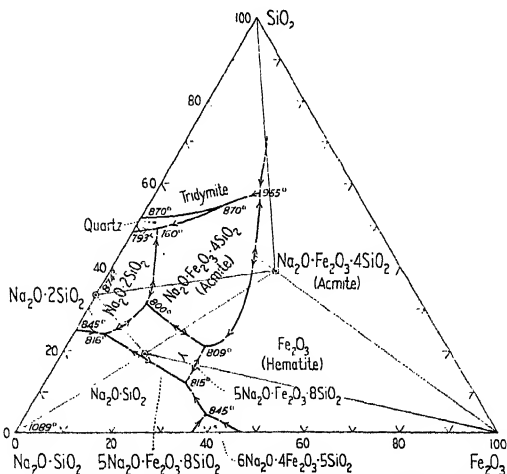


FIGURE 20. Equilibrium Diagram for the System; $Na_2O \cdot SiO_2 - Fe_2O_3 - SiO_2$, N. L. Bowen, J. F. Schairer, and H. W. V. Williams, *Amer. Jour. Sci.*, 5th Ser., 20, 405-55 (1930), p. 419. *J. Am. Ceram. Soc.* 16, 455 (1933).

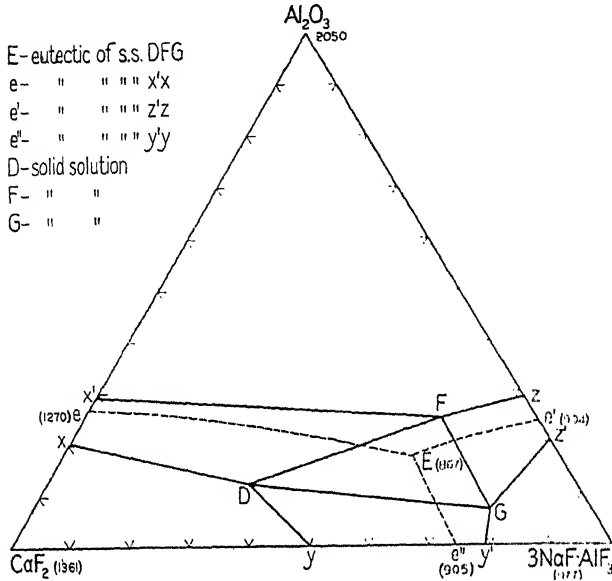


FIGURE 21. Equilibrium Diagram for the System; $\text{CaF}_2\text{-Al}_2\text{O}_3\text{-3NaF}\cdot\text{AlF}_3$, P. Pascal, Z. Elektrochem., 19, 610-13 (1913). J. Am. Ceram. Soc. 16, 455 (1933).

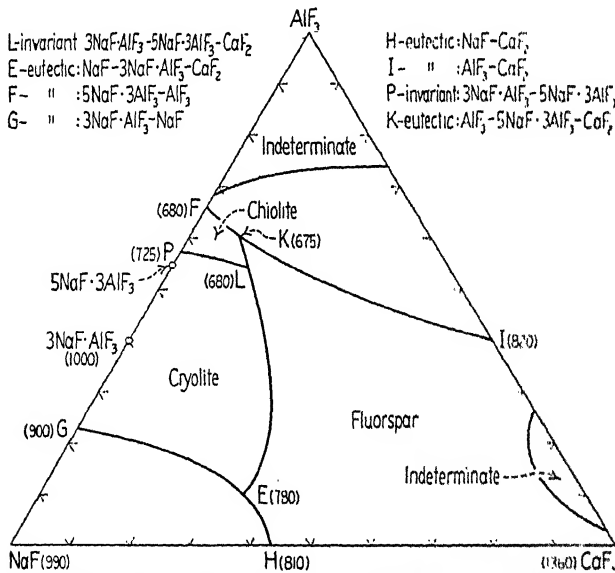


FIGURE 22. Equilibrium Diagram for the System; $\text{NaF-AlF}_3\text{-CaF}_2$, Fedotieff and Ilijnsky, Z. anorg. allgem. Chem., 129, 93-107 (1923). J. Am. Ceram. Soc. 16, 455 (1933).

$A=814^{\circ}$
 $B=995^{\circ}$
 $C=740^{\circ}$
 $D=765^{\circ}$
 $E_1=645^{\circ}$
 $E_2=665^{\circ}$
 $E_3=540^{\circ}$
 $E=775^{\circ}$
 $E_5=752^{\circ}$
 $E_6=764^{\circ}$
 $E_7=846^{\circ}$
 $E_8=793^{\circ}$
 $E_{10}=705^{\circ}$
 $FG=678^{\circ}$
 $HJ=678^{\circ}$
 $KL=590^{\circ}$
 $MN=573^{\circ}$
 $O=640^{\circ}$
 $PQ=870^{\circ}$
 $RS=1470^{\circ}$

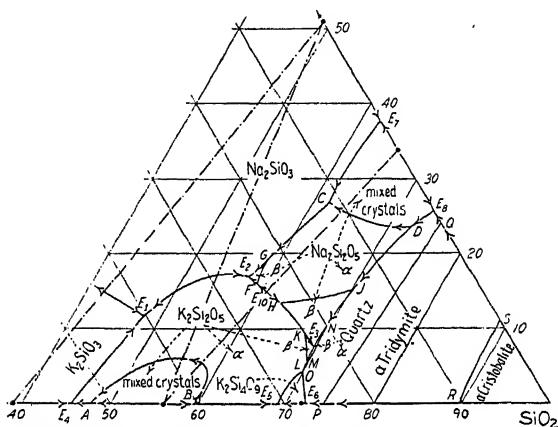


FIGURE 23. Equilibrium Diagram for the System; $K_2O \cdot SiO_2 - Na_2O \cdot SiO_2 - SiO_2$, F. C. Kraeck, Jour. Phys. Chem., 36, 2529-52 (1932), p. 2538. J. Am. Ceram. Soc. 16, 455 (1933).

Several investigators have studied the simple systems of two, three, and four components in an effort to develop more fusible and satisfactory enamels. Although handicapped by very meagre data on which to base such investigations, considerable progress has been made. Simpson⁴ has taken cone deformation eutectics of different systems and combined them in an effort to obtain even lower-melting combinations than these known eutectics. Combinations of ternary cone deformations were used by Simpson, with and without further additions of silica, to develop dry process cast iron enamels. Theoretically two eutectics combined will not necessarily form a lower melting mixture but the results of these investigations have been very instructive. It is a tremendous undertaking to study all possible combinations of as many different compounds as are present in enamels; therefore this information may never be complete. It is necessary, therefore, to study the most promising combinations based on the data which become available from time to time. The author has carried out extensive investigations on the use of simple systems as enamels, but only in a few cases have simple combinations of oxides approached satisfactory results. By adding to these simple systems, enamels can be developed, but the simplicity is then lost.

⁴ Harold E. Simpson, The Development of an Enamel on a Eutectic Basis; J. Am. Ceram. Soc. 13, 62-79 (1930).

PHYSICAL PROPERTIES OF ENAMEL GLASSES

All materials undergo changes in their physical properties with changes in temperature. Specific gravity, hardness, elasticity, brittleness, and the light effects such as refraction, reflection, and absorption are some of the properties changed. These changes are all important to the enameler as they concern the important properties of an enamel. Any enameler has seen changes of color, gloss, hardness, and elasticity as the enamel cools. Contraction and expansion are outward expressions of the volume changes. In glasses and enamels it is possible, with a fair degree of accuracy, to calculate many of these properties from the chemical composition. It has been shown that the values of certain of these properties are approximately additive.

If a glass contains a number of oxides, A, B, C, etc., the percentage weights of which are, respectively, P_A , P_B , P_C , etc., and the constants of the properties for each, respectively, X_A , X_B , X_C , etc., the following formula may be applied to obtain the specific property of the glass,

$$K = P_A X_A + P_B X_B + P_C X_C, \text{ etc.},$$

where K represents the specific property. In some glasses the accuracy of such a calculation is very great, but in others an approximation only is obtained. This is true, because the presence of one element in a glass may influence the effect of another, a fact which explains why the values determined by different investigators do not agree. They have been determined on different types of glasses, therefore, in each case the conditions are different. An example of the influence of borax on the coefficient of thermal expansion of sheet iron ground coat enamels is shown in Figure 25.

Thermal Expansion. The literature contains many investigations of the relationship between composition and the physical properties of glass, but few of the glasses studied could be considered to be of the enamel type. The first extensive systematic investigation of the problem was published by Winkelmann and Schott,⁵ who found that certain oxide factors could be used to calculate the approximate cubical coefficient of thermal expansion of glasses. These factors were based on an extensive investigation, and for convenience in calculation were made to represent the contribution of one per cent of the given oxide to the total expansion of the glass. Although these factors showed considerable variation, even with the glasses investigated, they have been assumed by many to be more accurate than was ever intended by Winkelmann and Schott.

⁵ Wiedemann's *Annalen* Bd. 51, 731 (1894).

This work was later supplemented by an investigation of enamel glasses by Mayer and Havas,⁶ who added the factors for many more of the oxides than the original work covered. It is the most complete investigation ever undertaken and the factors are the best available for enamel glasses.

English and Turner⁷ calculated a new set of factors, based on the assumption that silica carried the expansion of fused quartz into glass. These differ considerably from those previously published.

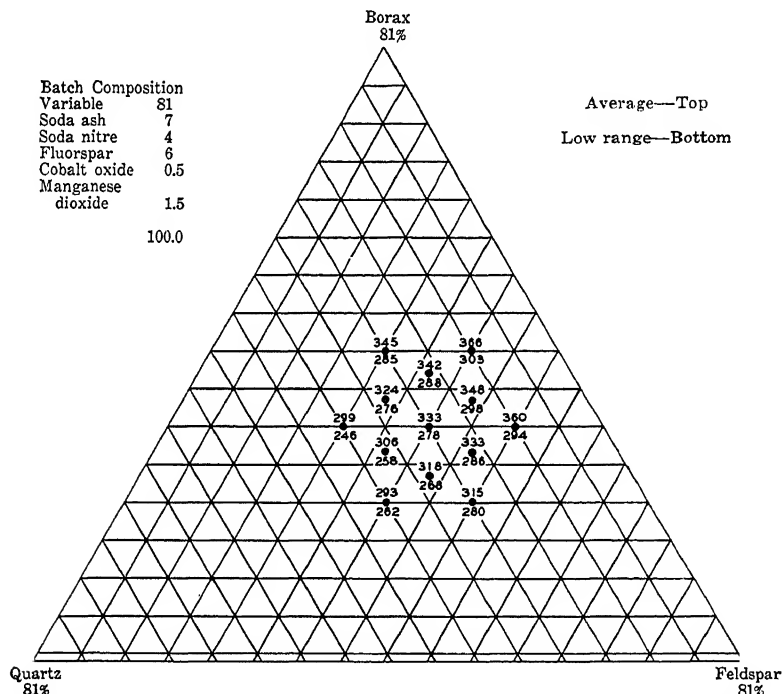


FIGURE 24. Low Temperature Range and Average Expansions of Typical Sheet Iron Ground Coats:

Hall,⁸ working at the National Bureau of Standards, determined factors for some of the common glaze oxides.

Fetterolf and Parmelee,⁹ at the University of Illinois, worked on the same basic assumption as English and Turner, thoroughly investigating the action of several oxides over a wide range of composition.

⁶ Sprechsaal 42, 497 (1909); 44, 188, 207, 220 (1911).

⁷ J. Soc. Glass Tech. 4, 115 (1920); 5, 121 (1921).

J. Am. Ceram. Soc. 10, 551 (1927); 12, 760 (1929).

⁸ E. P. Hall. J. Am. Ceram. Soc. 13, 182 (1930).

⁹ L. D. Fetterolf and C. W. Parmelee. J. Am. Ceram. Soc. 12, 193 (1929).

TABLE 2. FACTORS FOR CALCULATING THE PROPERTIES OF GLASSES AND ENAMELS

Composition	THERMAL EXPANSION				Heat Conductivity P. d. F.	Density		Tensile Strength W. d. S. Kg. per sq. mm.	Crushing Strength W. d. S. Kg. per sq. mm.	Elasticity C. d. T.	Hardness Auerbach	Specific Heat H. d. C.
	M. d. H. $\times 10^{-1}$	W. d. S. $\times 10^{-5}$	E. d. T. $\times 10^{-5}$	P. d. P. $\times 10^{-5}$		Density						
						W. d. S.	Ballie					
SiO ₂	0.8	0.8	0.15		0.0220	2.3	2.24	0.09	1.23	40	+ 3.32	0.001913
Al ₂ O ₃	5.0	5.0	0.42		0.0220	4.1	2.75	0.05	1.0	120	+10.1	0.002272
B ₂ O ₃	0.1	0.1	—1.98		0.0160	1.9	3.00	0.065	0.90		+ 0.75	
Na ₂ O	10.0	10.0	12.96	12.5	0.0160	2.6	3.20	0.02	0.52	110	— 2.65	0.002674
K ₂ O	8.5	8.5	11.7		0.0010	2.8	3.20	0.01	0.05		+ 3.9	0.001860
PbO	4.2	3.0	3.18		0.0080	9.6	10.30	0.025	0.48		+ 1.45	0.000512
ZnO	2.1	1.8	2.1	1.85	0.0160	5.9	5.94	0.15	0.6		+ 7.1	0.001245
CaO	5.0	5.0	4.89		0.0320	3.3	4.30	0.20	0.20	240	— 6.3	0.001903
MgO	0.1	0.1	1.35			3.8	3.25	0.01	1.1	300		0.002439
BaO	3.0	3.0	4.2	5.7	0.0110	7.0	7.20	0.05	0.65		+ 1.95	0.000673
As ₂ O ₃	2.0 ²⁸	2.0				4.1	2.90	0.03	1.00			0.001276
P ₂ O ₅	2.0	2.0			0.0160	2.55		0.075	0.76		+ 1.32	0.001903
Sb ₂ O ₃	3.6											
SnO ₂	2.0											
TiO ₂	4.1											
ZrO ₂	2.1											
NaAlF ₆	7.4											
NaF	7.4											
AlF ₃	4.4											
CaF ₂	2.5											
Cr ₂ O ₃	5.1											
CoO	4.4											
CuO	2.2											
Fe ₂ O ₃	4.0											
NiO	4.0											
MnO ₂	2.2											

F. & P.—Fetterolf and Parmelee, J. Am. Ceram. Soc. 12, 214 (1929). P. & F.—Paalborn and Focke, Jena Glass.
 E. & T.—Corrected to English and Turner, J. Am. Ceram. Soc. 12, 760 B.—Baillie, J. Soc. Chem. Ind., 40, 141 (1921).
 (1929). C. & T.—Clark and Turner, J. Soc. Glass Tech. 3, 200 (1919).
 W. & M.—Winkelmann and Schott, Jena Glass. H. & C.—Hodkin and Cousen, Glass Technology, Constable & Company, Ltd. (1925).

Gehlhoff and Thomas¹⁰ did considerable work on the expansion of glasses and pointed out the fact that factors for calculation are accurate only in limited fields of composition.

Harrison¹¹ studied sheet iron ground coat enamels and developed a set of factors, which check very well with the results of actual determinations with the interferometer.

Table 2 shows the factors determined in these investigations of the thermal coefficient of expansion.

To check these factors for accuracy in sheet iron ground coats, the author and R. K. Smith¹² determined the thermal coefficients of

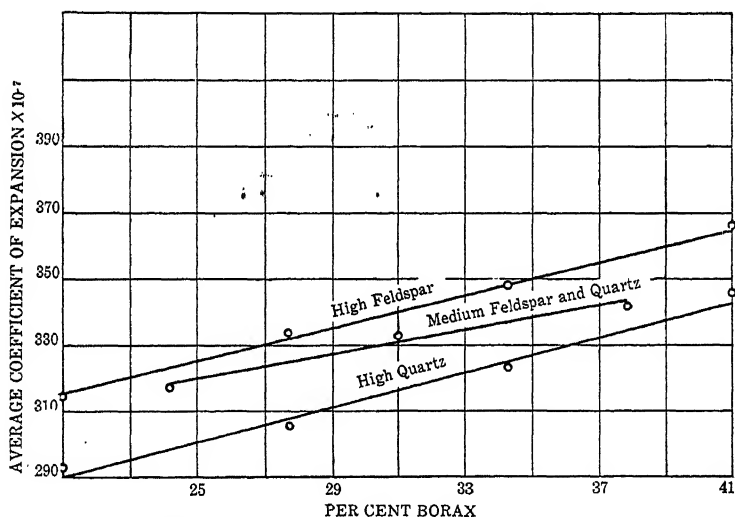


FIGURE 25. Effect of Borax on the Average Coefficient of Expansion.

expansion of a systematic variation of compositions, which are indicated in Figure 24. These results show by their agreement with calculated value, that the factors of Mayer and Havas are most suitable for this type of enamel and are fairly accurate. From these data the effect of borax on the average coefficient of expansion is plotted in Figure 25. This figure shows that an increase of borax always raises the expansion coefficient, but it also shows that the rate of increase, as indicated by the different slopes of the curves, depends upon not only the amount of borax but also the other constituents present. Silica and

¹⁰ G. Gehlhoff and M. Thomas. *Zeitschr. f. Technische Physik*, p. 102 (1926).

¹¹ W. N. Harrison. Bureau of Standards. Reported at the Meeting of the Am. Ceram. Soc., February, 1933.

¹² J. Am. Ceram Soc. 16, 328-337 (1933).

feldspar, plotted similarly, give approximately parallel lines, showing that their factors are not greatly influenced by the other constituents present in such compositions as sheet iron ground coats.

The thermal expansions of sheet iron cover enamels cannot be accurately calculated by the factors of Mayer and Havas, as shown by the results of actual determinations.¹³ The compositions used in this investigation and the results obtained are shown in Figure 26.

In this figure the points marked Logical Fluorides were determined by calculating the batch compositions to the melted compositions on

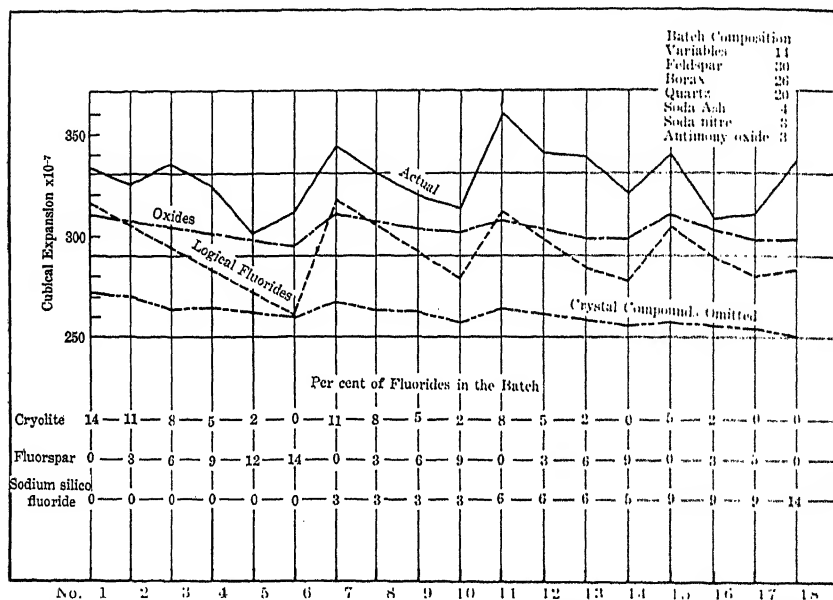


FIGURE 26. Comparison of Actual Values and Calculated Values for the Thermal Expansion of Sheet Iron Cover Enamels.

the basis of one hundred per cent. Cryolite was assumed to be broken down on entering the melt, contributing sodium fluoride, aluminum oxide, and fluorine gas. Sodium silicofluoride was assumed to be broken down into sodium fluoride, silica, and fluorine gas. All other raw materials were considered as the simple oxides. Each oxide or fluoride was multiplied by its expansion factor, and the sum of these quotients gave the theoretical cubical coefficient of thermal expansion.

The results marked Oxides were obtained by assuming that the

¹³ A. I. Andrews and E. E. Howe. J. Am. Ceram. Soc. 17, 288 (1934).

fluorine was completely volatilized, and calculating the remaining elements as oxides.

Assuming that the compounds, sodium fluoride, calcium fluoride, and antimony pentoxide, do not affect the expansion of the glass; they were subtracted from the composition, the remaining glass calculated to one hundred per cent and the factors applied. These results are labeled Crystal Compounds Omitted. Although this assumption has often been made in the calculations of the expansions of enamels, the results would indicate that it is not well founded.

Several other variations from these three types of calculations were made, but the variations were slight and the results are not shown.

Figure 26 shows that all calculated coefficients of expansion of the enamels containing fluorides were low compared to those actually observed.

Although the average of the oxide values for the different enamels is closer to the actual values, those obtained by calculating the logical fluorides more closely parallel the actual values and are, therefore, although low, more indicative of the variation from one enamel to another.

Since the Logical Fluoride values parallel the observed values fairly closely, expansion factors for sodium fluoride and calcium fluoride were calculated, which for the enamels studied would yield approximately the actual values. These new factors, calculated from enamels number seven and eight, were CaF_2 4.1 and NaF 10.0. These factors are not proposed to replace those of Mayer and Havas, since they are based on only a limited amount of data. Only the values for calcium fluoride and sodium fluoride were arbitrarily raised, since the Mayer and Havas factors have been shown to check very closely in ground coat enamels with smaller percentages of fluorine compounds. It should be further understood that, although these new factors are applied to fluorides, the actual cause for the increased expansion may be due to the effect of the fluorides on the properties of the other materials.

Further examination of Figure 26 shows that the trend of increasing expansion is in the direction of increasing sodium silicofluoride (see points one, seven, and eleven). This is contrary to the expected results. One possible explanation of this is that the sodium silicofluoride, being relatively unstable, is more completely broken down, thus giving a greater amount of sodium fluoride than that obtained from cryolite.

There is very little difference between the expansion coefficients of the individual enamels, since actual values lie between 300 and 360×10^{-7} cm. per centimeter per degree Centigrade. Nevertheless, the trend of decreasing expansion with increasing fluorspar may be noted when replacing either cryolite or sodium silicofluoride. In the case of cryolite replacing sodium silicofluoride, the expansion tends to reach a maximum at a point about midway between the two and then decreases on either side of this point. The fact that fluorspar decreases the expansion might be expected, since it is apparent that an addition of either cryolite or sodium silicofluoride means an addition of soda with a factor of ten, while the factor for lime is five.

Figure 27 shows typical expansion curves for enamels, the values being indicated by the slopes of the curves at the different tempera-

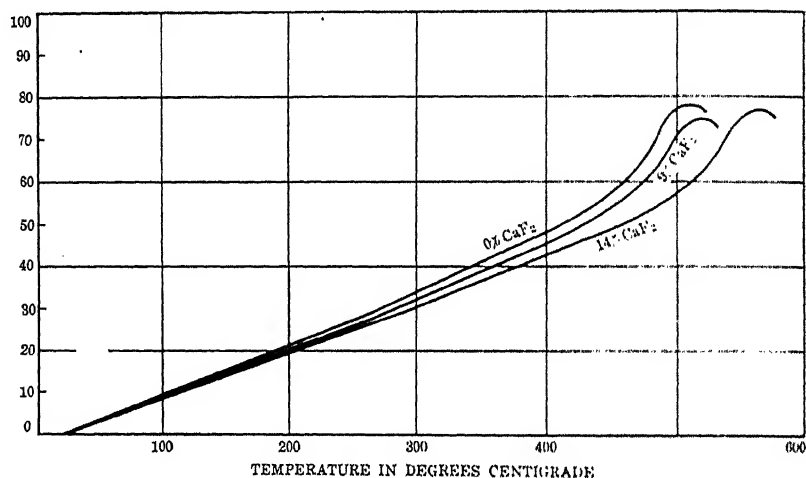


FIGURE 27. Typical Expansion Curves for Enamels.

tures. The breaks in the curves above 490°C are caused by the softening or fusion of the enamel.

The properties other than expansion, such as density, tensile strength, elasticity, hardness, specific heat, thermal conductivity, and crushing strength, have been investigated to a limited extent. They are valuable as approximations and should be used as such.

Density. The reciprocal of the density, or specific volume, is the additive property which can be used in calculating density, and the

results are fairly reliable. Winkelmann and Schott's ¹⁴ formula for density is:

$$\frac{100}{D} = \frac{p_1}{v_1} + \frac{p_2}{v_2} + \frac{p_3}{v_3}$$

where D = density of the glass,
 p = percentage of the oxide,
 v = density of the oxide used
 (calculated from glass).

Elasticity. Young's modulus for soda-lime glasses was determined by Clark and Turner ¹⁵ by means of the following formula:

$$E = p_1e_1 + p_2e_2 + p_3e_3$$

where E = Young's Modulus for glass,
 p = percentage of the oxide present,
 e = factor for the oxides used.

Tensile Strength. Winkelmann ¹⁶ calculated the tensile strength of glasses successfully by means of the following formula:

$$T = p_1t_1 + p_2t_2 + p_3t_3$$

where T = tensile strength of the glass,
 p = percentage of the oxide,
 t = factor for the oxide used.

Hardness. Although hardness is not as easily determined as some of the other properties, the following represents the method used by Auerbach ¹⁷:

$$H = p_1h_1 + p_2h_2 + p_3h_3$$

where H = hardness of the glass,
 p = percentage of the oxide,
 h = factor for the oxide.

Specific Heat. The specific heat may be calculated from the formula:

$$S = p_1s_1 + p_2s_2 + p_3s_3$$

where S = specific heat of the glass,
 p = percentage of the oxide,
 s = factor for the oxide.

¹⁴ Jena Glass, Hovestadt, translated by J. D. and A. Everett, London (1902).

¹⁵ J. Soc. Glass Tech., 3, 260 (1919).

¹⁶ Jena Glass, Hovestadt.

¹⁷ Hodkin and Cousen, Textbook of Glass Technology. D. Van Nostrand (1925).

Thermal Conductivity. Paalhorn¹⁸ determined factors for the calculation of the thermal conductivity:

$$C = p_1c_1 + p_2c_2 + p_3c_3$$

where C = thermal conductivity,
 p = percentage of the oxide,
 c = factor for the oxide.

Crushing Strength. Winkelmann and Schott¹⁹ used the following formula for the calculation of the crushing strength of glasses:

$$CS = p_1cs_1 + p_2cs_2 + p_3cs_3$$

where CS = crushing strength of the glass,
 p = percentage of the oxide,
 cs = factor for the oxide.

Although the calculated values often give only approximations, they are quite useful in research and practice. The factors for the different properties are given in Table 2 on page 40.

OPACITY

Theory. The opacity of enamels is caused by the phenomena of *reflection, refraction, and diffraction* of the light by particles imbedded in the matrix of glass. This results in a diffusion of the light, which is termed opacity, as applied to enamels. The light falls upon the enamel in parallel rays, and by means of these phenomena the rays are diffused in all directions, destroying the transparency of the enamel. To produce this diffusion of light, the index of refraction of the imbedded particles must be different from that of the glass.

The light is diffused by reflection from the enamel surface and also from the suspended particles, the latter being the more important; crystals and small particles giving greater diffusion of the light than large round particles.

As light passes from a medium of one density to a medium of another density it is refracted, depending on the differences in the densities, and the direction of propagation of the ray is changed. To give opacity, the index of refraction of the suspended particles must be different from that of the glass, thereby producing refraction of the light rays at every interface. This results in a disorderly change in the paths of light and produces diffusion. Again, as in the case of reflec-

¹⁸ Jena Glass, Hovestadt.

¹⁹ *Ibid.*

tion, the particles of irregular shape and small size produce the greatest diffusion.

The phenomena of reflection and refraction work together in producing diffusion of the light in enamels. If the light strikes the surface of a particle at greater than the limiting angle, it is reflected, and if it strikes the surface at less than the limiting angle, it is refracted, both phenomena contributing to the diffusion of the light.

It is, therefore, evident that the more interference the light meets with in being reflected and refracted through the glass, the greater will be the diffusion and the opacity. To produce this effect, the particles should be highly dispersed and of irregular shapes and sizes. The nature of the ideal combination of sizes and shapes, however, cannot be stated.

If the sizes of the particles, however, approach the dimensions of light rays, the phenomena of reflection and refraction no longer exist, but the light becomes diffracted. The diffraction of light increases with a decrease of particle size below that of light waves to a maximum, whereupon diffraction decreases as the particles get still smaller.

It is, therefore, evident that a maximum of opacity is theoretically reached, when the larger particles are small enough to give the greatest possible opacity by reflection and refraction, and the smallest particles are large enough to give greatest diffraction opacity.

When the light is reflected, refracted, and diffracted, the white light is decomposed into colors, but the amount of diffusion produced in enamels generally obscures this phenomenon.

Types of Opacity. Since suspended particles of either higher or lower optical density than the glass may produce opacity, there are different types to be considered.

Opacity produced by particles of a higher index than the glass may be divided into (a) insoluble particles, (b) crystallites, and (c) immiscible constituents, (d) gas bubbles.

Insoluble particles added to the mill batch of an enamel often represent the insoluble type. Here the opacifier is added to the frit and milled to a fine state of dispersion. In fusing the enamel these opacifying particles are suspended in the glass in a finely divided, dispersed form and, therefore, give opacity to the enamel.

In the second type of opacity the particles are formed by devitrification, or crystallization. Such opacity is usually developed in smelting the frit, the compounds either forming in the smelting operation or crystallizing out of the glass on cooling. The jewelry enamels using arsenic oxide as the opacifier illustrate crystallization on cooling and

the antimony enamels, in which antimony pentoxide is formed during the smelting, are illustrative of the other type.

The production of good opacity by crystallization is dependent upon the spontaneous formation of many crystal nuclei on cooling. If the crystallization is slow or progressive, large crystals form and the enamel tends toward either a mottled or a matt appearance.

If immiscible melts are formed in the glass the third type of opacity results.

A type of opacity in which the dispersed particles have a lower index of refraction than the glass, is that caused by minute gas bubbles. The opacity caused by bubbles alone is not usually strong but they undoubtedly contribute to the opacity of most opaque enamels.

These different types of opacity probably all contribute to the property in all enamels, some being more pronounced in one and others being more pronounced in another. It is only through the combination of these different types of opacity that we obtain the quality desired. In fact few enamels depend upon one material alone to develop good opacity.

TABLE 3
INDICES OF REFRACTION OF OPACIFIERS

Tin oxide.....	2.04
Zirconium oxide.....	2.13 2.19 2.20
Titanium oxide.....	2.50
Sodium fluoride.....	1.33
Calcium fluoride.....	1.44
Arsenic trioxide.....	1.73
Lead arsenate.....	2.14
Zinc sulphite.....	2.37
Zinc spinel.....	1.90
Antimony trioxide.....	2.09
Enamel glasses.....	1.50 1.55
Cryolite.....	1.34

The preceding theory of opacity explains this property of enamels as due to the differences in the indices of refraction of the enamel and the particles and also the sizes and the shapes of the suspended particles; but there is no way of predicting from the theories the opacity which will develop in an enamel under given conditions. Factors at present not understood make such predictions impossible, therefore actual trials are necessary in the study of opacity. The control tests are outlined in detail on page 341.

The X-ray Study of Opacifiers. The X-ray investigation of the compounds present in enamels has thrown considerable light on the actual compounds producing opacity.

Many theories concerning the cause or source of opacity in enamels and glasses are given by various writers, and some of the investigators have made X-ray determinations of opacifying compounds in glasses. Agde, Krause, and Lehmann²⁰ conclude that in using sodium fluoride (NaF) as the opacifying agent, the sodium fluoride (NaF) separates from the cooling solvent and produces turbidity; when aluminum fluoride is used, sodium fluoride is formed; with calcium fluoride the opacity is due to calcium fluoride and sodium fluoride. Enequist²¹ claims that the opal color is due to silicon tetrafluoride. Zschimmer²² states that the turbidity of opaque glass is the result of the precipitation of minute spheroids of fluorine compounds, principally sodium fluoride and calcium fluoride. Otremba²³ states that the opacity is due to crystals when cryolite is used and to fine air bubbles when fluorspar is employed. Bock²⁴ claims that fluorine has no influence whatever on the opacity of the resulting enamel. Ryde and Yates²⁵ state that the opacity of opal glasses has been attributed to alumina, aluminum fluoride, sodium silicofluoride, silica, silicon tetrafluoride, and aluminum silicates; however, their results show that the opacity of fluorine glasses is due either to sodium fluoride or calcium fluoride or both. Other writers and investigators have stated that opacity was caused by aluminum fluoride, silica, boric oxide, clay, oxides of tin, antimony, titanium, and zirconium (when compounds of these metals were used in the enamel), feldspar, colloidal silica or alumina, and by occluded gases. Randall, Rooksby, and Cooper²⁶ found cristobalite crystallites present in glasses of vitreous silica, wollastonite, and sodium borate. These glasses, however, were transparent, but are mentioned, because similar lines were obtained on the X-ray patterns of some of the opaque enamel glasses.

²⁰ G. Agde and H. F. Krause, Study of the Behavior of Fluoride Additions to Glasses and Enamels, *Z. angew. Chem.*, **40**, 525-33 (1927); *Chem. Abs.*, **21**, 2966 (1927); *Chem. & Ind.*, **46B**, 483 (1927); *Chem. Abs.*, **6**, 374 (1927); *Enamel Bibliography*, p. 1. G. Agde, H. F. Krause, and W. M. Lehmann, Behavior of Fluorides in Glasses and Enamels, *Z. angew. Chem.*, **40**, 804 (1927); *Chem. & Ind.*, **46B**, 654 (1927); *Enamel Bibliography*, p. 3; A. Agde and H. F. Krause, Effect of Fluoride Additions to Glasses and Enamels. Causes of Fluorine Losses During Smelting of Glasses and Enamels with Fluoride Additions, *Z. angew. Chem.*, **40**, 886-95 (1927); *Chem. & Ind.*, **46B**, 702 (1927); *Chem. Abs.*, **21**, 3434 (1927); *Enamel Bibliography*, p. 1.

²¹ E. Enequist, Chemistry of Opaque Glass and Enamel, *Chem. Eng.*, **10**, 54 (1909); *Chem. Abs.*, **3**, 2865 (1909); *Enamel Bibliography*, p. 110.

²² E. Zschimmer, Fluor-Opal and Theory of Opaque Glass Used in the Illuminating Industry, *Sprechsaal*, pp. 347-49, 364-66 (1930); *Chem. Abs.*, **24**, 3617 (1930).

²³ A. Otremba, Fluorine in Enamel Melting, *Keram. Rund.*, **34**, 158-60 (1926); *Ceram. Abs.*, **5**, 299 (1926); *Chem. Abs.*, **20**, 3339 (1926); *Enamel Bibliography*, p. 231.

²⁴ B. Bock, Importance of Fluorine in Enamels, *Chem. Ztg.*, **32**, 730-32; *Chem. & Ind.*, **27**, 900 (1908); *Chem. Abs.*, **2**, 2718 (1908); *Enamel Bibliography*, p. 29.

²⁵ J. W. Ryde and D. E. Yates, Opal Glasses, *Jour. Soc. Glass Tech.*, **10**, 274-94 (1926).

²⁶ J. T. Randall, H. P. Rooksby, and B. S. Cooper, Structure of Glasses; Evidence of X-Ray Diffraction, *Jour. Soc. Glass Tech.*, **14**, 219-29 (1930).

X-ray investigations on the compounds causing opacity have led to the following conclusions for certain dry process cast iron enamels:²⁷

Tin oxide, when used as the principal opacifying agent, was not dissolved by smelting and remained as crystalline tin oxide (SnO_2), giving opacity to the enamel. Fluorspar, when used with tin oxide, remained as crystalline calcium fluoride in smaller quantities. Cryolite, when used with tin oxide, remained soluble in the enamel glass, and sodium fluoride did not crystallize to an extent sufficient to give a pattern on X-ray examination. When cryolite was used with fluorspar and tin oxide, crystalline sodium fluoride, as well as calcium fluoride, were present in the fused enamel.

In enamels containing commercial antimony oxide or sodium antimonate, crystalline antimony pentoxide (Sb_2O_5) was the compound causing opacity. The commercial antimony oxide was oxidized during smelting to the antimony pentoxide. It is assumed that sodium antimonate reacts in the enamel to form antimony pentoxide, and the sodium oxide goes to form part of the glass.

The crystalline compounds causing the opacity in enamels containing zirconium oxide, ZrO_2 ,* as the principal opacifier, with fluorspar or with cryolite as the secondary opacifier, were crystalline calcium fluoride, in the enamel containing fluorspar, and sodium fluoride in the cryolite enamel with an unidentified compound, which was neither pure zirconium oxide, nor zirconium silicate. It may have been some other form of the oxide or possibly a fluoride of zirconium. Zirconium enamels seemed to retain a greater per cent of their fluorine content than enamels containing the other opacifiers.

Sodium silicofluoride, fluorspar, cryolite, aluminum fluoride, or sodium fluoride, gave opaque glasses when used as opacifying agents alone. Sodium silicofluoride, when used as the principal opacifying compound with fluorspar as the secondary opacifier, gave an opaque enamel containing only crystalline calcium fluoride; while with cryolite as the secondary opacifier the enamel contained only crystalline sodium fluoride. When fluorspar was used alone, the enamel contained only crystalline calcium fluoride. When cryolite was used alone the enamel contained only crystalline sodium fluoride, the remainder of the cryolite being retained in the glass. With aluminum fluoride the opacity was caused by crystalline calcium fluoride when fluorspar was the secondary opacifier, and by sodium fluoride when cryolite was the

²⁷ Andrews, Clark and Alexander, *J. Am. Ceram. Soc.* 16, 385 (1933); Andrews and Breen, *J. Am. Ceram. Soc.* 16, 325 (1933).

* Added as "Opax."

secondary opacifier. No crystalline aluminum fluoride (AlF_3) was found in any of the enamels tested. When sodium fluoride was used as the principal opacifier with fluorspar as the secondary opacifier, both crystalline sodium fluoride and calcium fluoride were present, while with cryolite as the secondary opacifier only crystalline sodium fluoride was present. In all enamels in which the opacity was caused by either crystalline calcium fluoride, sodium fluoride, or both, the crystalline compounds were probably soluble in the enamel glass and crystallized on cooling, the degree of opacity depending upon the rate of cooling.

Sodium silicofluoride, fluorspar, and cryolite aided in the development of opacity when used with tin oxide, antimony oxide, or sodium antimonate. They did not cause opacity in the presence of these metal oxides, except in the case where fluorspar and cryolite were present with tin oxide. The identification of crystalline calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, in the fused enamel was unexpected and, although the patterns obtained seemed conclusive, more work should be done on this type of enamel before final conclusions are drawn.

The following are results obtained from an X-ray study of sheet iron cover enamels:

The variations of feldspar, borax, and quartz in the enamel composition had no effect on the identity of the crystalline compounds showing opacity. It is quite probable, therefore, that the composition of the enamel glass has little if any effect on the nature of the crystalline compounds causing opacity.

The variations of fluorspar, antimony oxide, and cryolite, showed that each contributed to the crystalline compounds present in the enamel. Fluorspar was present in these sheet iron enamels as calcium fluoride, antimony oxide was present as antimony pentoxide, and cryolite contributed crystalline sodium fluoride. If any one or more of these compounds were present in an enamel, the enamel was opaque. When tin oxide was added to the mill, crystals of tin oxide appeared in the X-ray pattern. The zirconium oxide (Opax) enamel, however, did not show the presence of zirconium oxide and, although the enamel was made opaque, no crystalline particles showed in X-ray tests.

The transparent frits made by smelting the opacity out of the enamels showed no crystalline compounds, although cryolite, fluorspar, antimony oxide, and tin oxide were present in the raw batch. This indicates that the opacity obtained by these compounds was caused by the crystallites.

FUNDAMENTALS OF COLOR

The light coming from the sun is white light, containing all of the colors of the spectrum. As this white light falls on objects, a portion of it is absorbed or transmitted through the object and the remainder is reflected. Different objects have different absorbing characteristics, therefore the light reflected from various objects differs. If an object absorbs or transmits all except red light rays, then these red rays are reflected and we state that the object is red. When observing the object by allowing the light to fall on it, we get only the sensation of the light rays reflected. If we allow the light to pass through the object, we may get an entirely different color sensation, for we are then observing the transmitted rays; that is, the original rays minus those absorbed and reflected by the object as the light passes through it.

The character of the light used for such observation of reflected or transmitted light often influences the color, since rays not present in the original light cannot be reflected or transmitted. Thus, a yellow light falling on an object reflecting only red light will give the object the appearance of being black, while, if white light were used, the red rays would have been reflected and the object would have appeared red in color.

The light from the sun containing all the rays of the visible spectrum is white light, which vibrates in wavelengths of 3900 to 7700 angstrom units.* The different colors represent different ranges of vibrations within these limits of the visible spectrum, as shown in Table 4.

TABLE 4
VISIBLE SPECTRUM

Violet.....	3900-4220 A.U.
Blue.....	4220-4920 A.U.
Green.....	4920-5350 A.U.
Yellow.....	5350-5860 A.U.
Orange.....	5860-6470 A.U.
Red.....	6470-7700 A.U.

Thus, violet represents the shortest rays and red the longest. If the vibrations are shorter than the violet, they are not visible to the eye and enter the field of ultra-violet, x-rays, γ -rays and, finally, cosmic rays. If the vibrations are longer than the red rays, they enter the field of the infra-red rays, solar radiation, Hertzian rays, radio rays, and, finally, the electric rays.

$$* 1 \text{ A.U.} = 10^{-8} \text{ cm.} = \frac{1}{100,000,000} \text{ cm.} = \frac{1}{254,000,000} \text{ inch.}$$

We are at present particularly interested in the visible spectrum, which includes the colors sensitive to the eye. Of these colors, red, yellow, and blue are considered the primary colors, all others being combinations of these three colors with additions of black or white to vary the shade or tint.

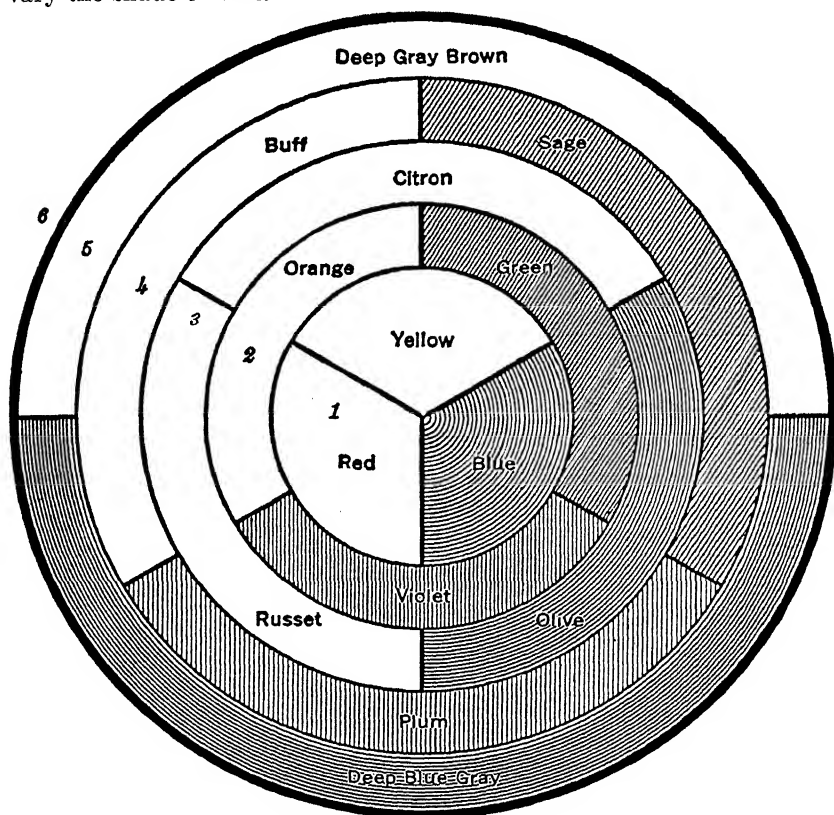


FIGURE 28. The Color Circle.†

Colors have three general characteristics: hue, brightness, and strength. Hue is the color. Brightness represents the position between black and white. Additions of white control the tint and additions of black, the shade. Strength represents the power of the color or its freedom from gray. W. J. Miskella²⁸ gives two diagrams, which very clearly explain these different properties of colors.

In Figure 28 the colors are shown in what is called the chromatic or color circle. In the center are shown the three primary colors: red,

²⁸ Practical Color Simplified; Finishing Research Laboratories (1928).

† W. J. Miskella, Practical Color Simplified; Finishing Research Laboratories (1928).

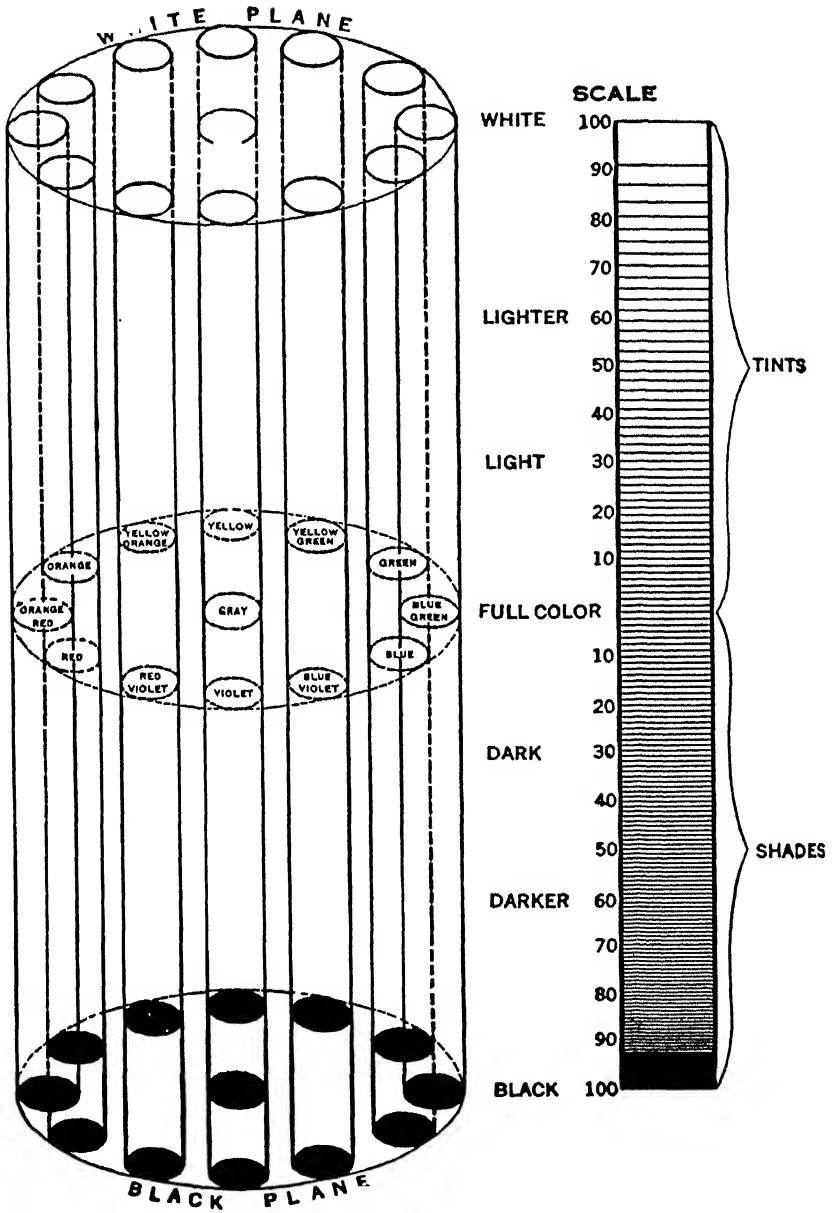


FIGURE 29. The Color Cylinder.†

† W. J. Miskella, *Practical Color Simplified*; Finishing Research Laboratories, Chicago (1928).

yellow, and blue. The second circle represents the combinations of two of these colors, orange for red and yellow, green for blue and yellow, and violet for red and blue. The tertiary colors (third circle) are combinations of the secondary, the quaternary (fourth circle) combinations of the tertiary and so on until we reach the outer circle, which is a combination of all or black.

Figure 28 represents only combinations of pure color or hues, but Figure 29 shows the relation to black and white additions. The primary and secondary colors are arranged in a circle with proper relation to one another and gray at the center representing combinations of all. Above this central plane in the diagram labeled full color, are additions of white, which give the various tints of the colors, until the upper plane is reached and white predominates. Below the central plane showing full color, progressive additions of black are represented, which give the different shades until the lower plane is reached and black predominates.

These fundamental facts concerning color aid greatly in the understanding of the properties of color and their application.

The blending of colors in enamels, however, offers difficulties in addition to those based on color alone, because of the chemical reactions which may take place. For example, it is not safe to depend upon a red and a yellow forming an orange, or a blue and a yellow forming a green. These principles of color blending can be used as an aid in obtaining new colors, but trial batches must always be made to check the results. As outlined on page 342, the spectrophotometer or color analyzer can be used to determine the combinations actually present in a specimen. By this means, and a cut-and-try method the desired color can be obtained.

For further information on color refer to the Munsell Color Books.²⁹

²⁹ Munsell Color Co. Inc., Baltimore, Md.

CHAPTER 4

Cast Iron, Sheet Iron, and Steel

Although the enameler does not usually have direct control over the making of the metal stock for enameling, he should be familiar with the operations involved, the compositions, and the properties. The success of enameling depends to a considerable degree on the metal base to which the enamel is fused. The compositions of irons which can be enameled cover a wide range from commercially pure iron to fifty-hundredths carbon steels and cast irons, but no great variation can be tolerated for a given enamel and enameling process. A uniform grade of iron is very important. The use of low grade iron for enameling is not economy, since a great many defects, such as blisters, fishscale, and chipping may be caused by the iron.

In the cast iron enameling industry the castings are often made in the same factory organization in which they are enameled. This permits the maximum cooperation between the foundry and the enameling shop, which is a great aid to efficiency. The importance of this cooperation is not always appreciated by the management, but it is becoming better known and the most modern plants require it. These two departments must work together for the good of the whole manufacturing process. The following pages should aid the foundry man, as well as the enameler, to a better understanding of the requirements for enameling, and the defects characteristic of poor castings.

The sheet metal enameler does not usually have control over the manufacture of the sheets, but he can purchase them from the steel companies giving the most suitable product and service. Methods of forming the ware from the sheets, however, are usually within his influence and should be carried out with the view to enameling in mind.

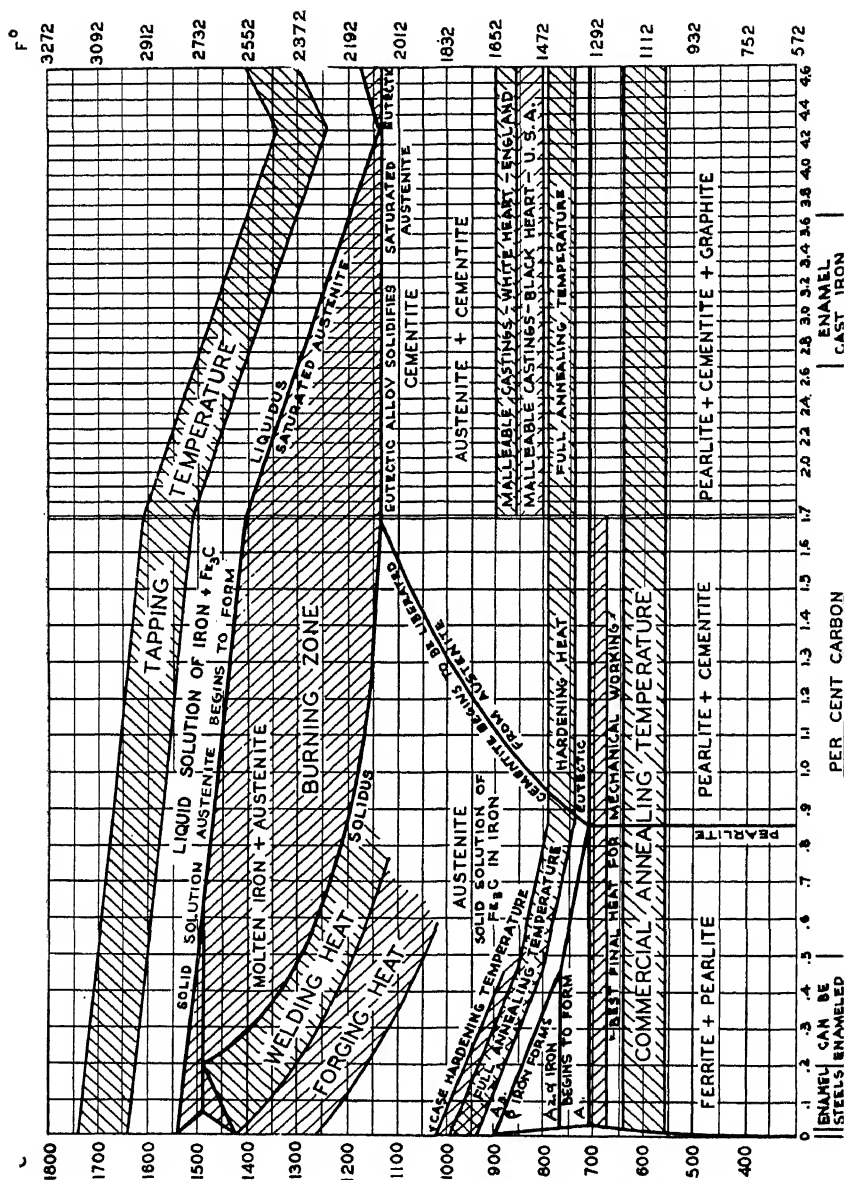
The design of the shapes of both cast iron and sheet iron ware is important to successful enameling. The shape, the thickness, the angles, and projections should all be designed to aid the enameling operation.

FUNDAMENTALS

Cast iron, sheet iron, and steel compositions differ chemically in their contents of carbon. The other constituents, silicon, manganese, sulphur, phosphorous and the less common elements, are specific in their action and are not closely related to this general classification.

The iron-carbon temperature relations have been investigated

CAST IRON, SHEET IRON, AND STEEL



extensively and are shown on the diagram in Figure 30. This information is fundamental to the metallurgist and explains many of the characteristics of iron. The enameler should have a thorough understanding of it.

The diagram (Figure 30) shows the equilibrium conditions of all combinations of iron and carbon between pure iron and a cast iron containing 4.6 per cent of carbon and 95.4 per cent of iron. Higher percentages of carbon do not occur in commercial irons. The vertical axis represents temperature, the Centigrade scale being given at the left and the Fahrenheit scale at the right. On studying this system, it will be noted that there is one eutectic at 4.25 per cent of carbon, which melts at 2060° F.

The commercially pure enameling iron, which is used for sheets, has a composition very close to one hundred per cent pure iron. The steels have higher percentages of carbon up to 1.7 per cent, and the cast irons contain from 1.7 per cent up. The steels are grouped into two classes, the hypo-eutectoid steels and the hyper-eutectoid steels. The soft steels, which are quite malleable, contain low carbon; the mild, medium carbon, and the hard steels contain high carbon of the hyper-eutectoid range. Enameling steels usually contain less than 0.20 per cent of carbon, but in rare cases may go as high as 0.50 per cent carbon. As the carbon content increases in these higher ranges, there is a decided tendency toward blistering.

The cast irons used for enameling may contain between 2.8 and 3.7 per cent of carbon, but usually contain from 3.25 to 3.6 per cent.

The form in which the carbon is present in enameling irons is of great importance. Below the solid solution area of the diagram in Figure 30, it will be noted that there are many modifications, the equilibrium areas of which are outlined. These modifications determine the structure, the properties, and the enameling characteristics of the iron to a marked degree. It is impossible, in this short discussion of the fundamentals, to more than touch on the extensive information which is available in the many good books on the metallurgy and metallography of iron. It will be noted, however, that below the solid solution and molten iron area, of the steel range, cementite (Fe_3C) is formed in a solid solution, as austenite (Table 5). Below this area, there is a eutectoid point where solid solution (austenite), cementite (Fe_3C), and pure iron (ferrite) are in equilibrium with each other. With carbon contents greater than this eutectoid (.85% carbon), cementite crystallizes out of the solid solution, and with lower per cents of carbon, ferrite crystallizes out of the solid solution. The ferrite goes

through several modifications, α , β , and γ , on heating or cooling. In any case, the solid solution is changed to the pearlitic structure on still further cooling. In the cast iron area, the eutectic (4.25 per cent carbon) crystallizes at 2060° F with austenite and cementite present. At lower temperatures the austenite disappears and pearlite appears with the crystallization of cementite and graphite.

The rate of cooling determines the amount of inversion which takes place in the iron. Rapid cooling tends toward a solid solution of austenite, while slow cooling permits the inversion to take place. The structure of the iron and its physical and enameling properties are,

TABLE 5
THE CONSTITUENTS OF IRON AND THEIR PROPERTIES

<i>Name</i>	<i>Composition</i>	<i>Micro Appearance</i>	<i>Tensile Strength</i>	<i>Other Properties</i>
Cementite	Fe ₃ C	Light	5000 lbs.	
Ferrite α	Fe	Light	40,000 to 50,000 lbs.	Magnetic and Ductile
Ferrite β	Fe	Light		Non-magnetic
Ferrite γ	Fe	Light		Dissolves car- bon or Fe ₃ C
Austenite	Variable Solid Solution	Medium		
Pearlite	0.85% C Fe ₃ C & Fe	Dark	125,000 to 130,000 lbs.	

therefore, influenced by the rate of cooling. Even the temperature of firing (less than 1700° F) has an influence on the structure of the iron, as shown by a comparison of Figures 33 and 34.

The accompanying photomicrographs show the structures of a typical enameling iron, a mild steel, cast iron before enameling, and cast iron after enameling.

The effect on the properties of the iron can be readily realized by comparing the properties of the individual constituents in Table 5.

CHEMISTRY OF CAST IRON

Although cast iron is principally iron and carbon, its composition is not simple. It practically always contains, in addition, manganese, silicon, sulphur, and phosphorus, which even in small amounts affect

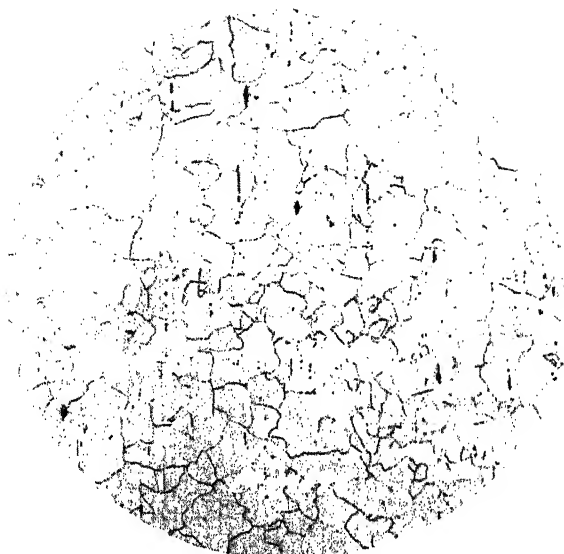


FIGURE 31. The Microstructure of Ingot Iron.* (100 \times , etched in 3% Nital.) This photomicrograph represents the structure of ingot iron enameling stock. The structure consists entirely of ferrite.

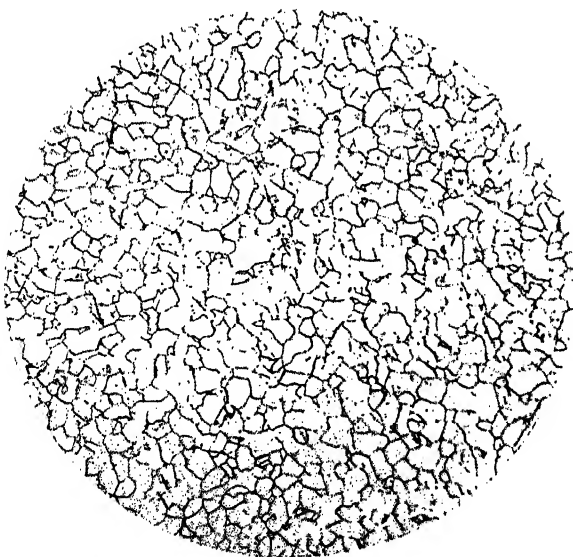


FIGURE 32. The Microstructure of Mild Steel.* (Etched in 3% Nital.) The structure represented here is that of mild steel of the following composition: C—.05, S—.035, Si—trace, P—.005, Mn—.30. The structure is ferrite and pearlite.

* These photomicrographs, Figures 31 to 34, were furnished by Dr. J. J. Canfield of The American Rolling Mills Company (1934).

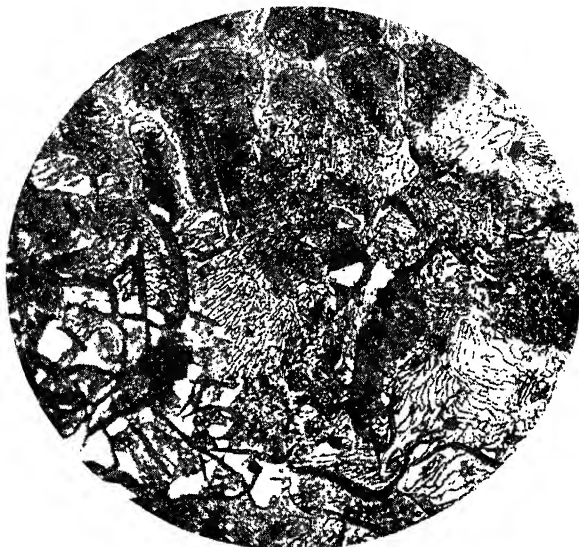


FIGURE 33. The Microstructure of Enameling Cast Iron.* (500 \times , etched in 3% Nital.) Cast iron enameling metal, consisting principally of pearlite with some free ferrite, some graphite, and steadite. The sample was taken from a light weight unenameled casting.

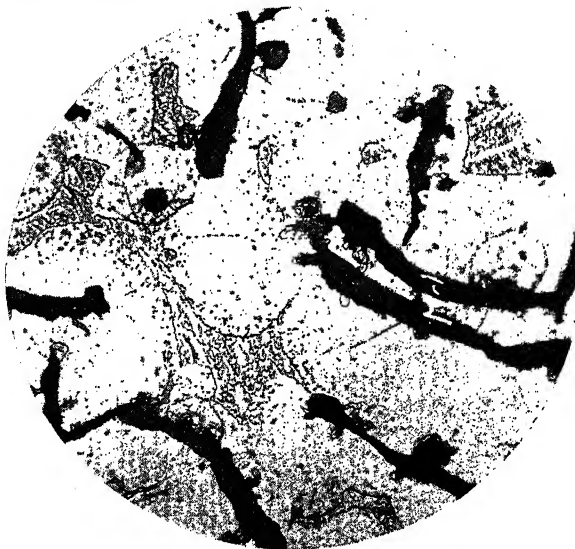


FIGURE 34. The Microstructure of Enameling Cast Iron After the Enamel Was Fired.* (500 \times , etched in 3% Nital.) This is the same metal as that shown in Figure 33, except that the enamel was fired on it in a continuous wet process furnace. The rate of cooling was slow, therefore, the carbon is practically all present as graphite, with very small amounts of combined carbon existing along the graphite plates. The ferrite contains fairly large amounts of steadite.

The photomicrograph of a dry process cast iron shows a similar structure.

the properties, both during manufacture and in the finished casting. The analyses of typical enameling cast irons fall within the limits shown in Table 6.

TABLE 6
PERCENTAGE CHEMICAL COMPOSITION OF CAST IRON FOR
ENAMELING PURPOSES

	<i>Limits</i>	<i>Ideal</i>
Total carbon.....	3.25-3.60	3.25-3.35
Graphitic carbon.....	2.80-3.20
Combined carbon.....	.22- .52
Silicon.....	2.25-3.00	2.50-2.60
Manganese.....	.45- .65	.45- .60
Phosphorus.....	.60- .95	.60- .70
Sulphur.....	.05- .10	less than .09

The structure of cast iron is, however, also important in the consideration of its enameling properties. Typical structures are indicated by the examples given in Table 7.

TABLE 7
PROXIMATE STRUCTURE OF CAST IRON FOR ENAMELING PURPOSES

	<i>I*</i>	<i>II*</i>	<i>III*</i>	<i>IV*</i>
Pearlite.....	52.56	45.92	49.6	57.7
Steadite.....	2.62	7.21	8.45	8.4
Graphite.....	2.80	2.80	2.8	2.7
Manganese sulphide.....	0.15	.23	0.15	0.2
Ferrite.....	37.87	43.84	39.0	31.0

Some of the compounds and elements occurring in the free state in the cast iron are listed by Malinovszky ¹ in Table 8.

TABLE 8
COMPOUNDS AND ELEMENTS PRESENT IN CAST IRON

<i>Constituent</i>	<i>Per Cent</i>	
	<i>I</i>	<i>II</i>
Graphitic carbon.....	3.24	3.19
Iron carbide.....	6.25	5.49
Manganese carbide.....	.32	.25
Iron phosphide.....	4.49	4.88
Iron silicide.....	7.53	8.66
Manganese sulphide.....	.15	.23
Iron.....	78.02	77.30

The composition, however, must meet the requirements of the foundry as well as the enameling shop. It must have sufficient fluidity to fill the mold completely without forming blow holes and slag spots.

* I and II. Malinovszky, J. Am. Ceram. Soc., 9, 808 (1928).

* III and IV. Krynitsky, J. Am. Ceram. Soc. 8, 620 (1925).

¹ Malinovszky, J. Am. Ceram. Soc. 9, 808 (1928).

It must utilize available scrap and must be an economically feasible composition.

Carbon. The carbon in the iron gives the characteristic properties of cast iron, the amount, however, being largely controlled by the raw materials and the foundry practice. White cast iron is low in uncombined graphitic carbon, which many enamellers consider an undesirable constituent for enameling irons. It was once thought that only white cast iron could be enameled, but most shops now use the gray cast iron. An increase in the combined carbon of cast iron results in an increase in the hardness of the iron. The combined carbon is present as cementite (Fe_3C) or dissolved in the pearlite or austenite of the iron. With an increase of the carbon content of cast irons the hardness, shrinkage, and brittleness increases. More than one per cent of combined carbon tends to weaken the casting and, if it exceeds three per cent as graphitic carbon, it becomes soft. The relative amounts of combined and uncombined carbon also depend upon the heat treatment.

Silicon. Silicon in cast iron tends to change the combined carbon into graphitic carbon, thereby softening the iron. If the iron is high in combined carbon, and the silicon does not reduce this latter constituent below one per cent, it has a strengthening effect in that it reduces the brittleness. It also tends to counteract the hardening effect of sulphur. If present in excess of three and one-half per cent, it changes the character of the iron entirely, the iron becoming silvery, brittle, and weak. Silicon improves the fluidity of the iron and, if it is not present in sufficient quantities, casting is difficult because of a tendency to form slag pits and blow holes. The silicon is expensive, but it is highly essential for producing good, malleable, fine-grain castings. Its effect is counteracted by both manganese and sulphur.

Manganese. Manganese tends to counteract the effect of sulphur in cast iron, thereby acting as a softener in amounts up to 0.50 per cent. In amounts over two per cent it hardens the iron. The manganese also acts to increase the solubility of carbon in the iron, making much higher percentages possible. In smaller amounts it toughens the iron, but where soft castings are desired, it must not exceed 0.50 per cent. It has a tendency to reduce the magnetic properties of the iron. Since pig irons are usually low in manganese, it must be added to them as spiegeleisen or ferro-manganese, which increases the cost.

Phosphorus. Phosphorus has little effect on iron, if added in amounts below 0.70 per cent, but, if added in larger amounts, it weakens it decidedly. Phosphorus decreases the shrinkage and, like

silicon, it increases the softness. It contributes considerably to the fluidity of the molten iron. Where intricate or thin castings are being made, phosphorus is a great aid, since the fluidity which it gives to the iron makes it possible to fill the mold perfectly.

Sulphur. Sulphur increases the hardness, brittleness, and shrinkage of the iron by reacting to form combined carbon. It weakens the iron and should never exceed 0.10 per cent, unless its effects are counteracted by other elements such as manganese. Its shrinkage is so great that it must be given special consideration in the making of patterns. If the silicon content is less than one per cent, the sulphur should not exceed 0.06 per cent because of the brittleness which it contributes.

Miscellaneous Elements. There are numerous other elements in some cast irons, many of which have little effect on the properties. Nickel softens and strengthens cast iron, producing a fine grain. Aluminum softens and weakens gray iron, but white iron is strengthened by 0.2 to 1.0 per cent. Vanadium alloys with the iron and acts as a deoxidizer, strengthening it. Chromium hardens the iron, and titanium strengthens it, also acting as a deoxidizer.

Although it is true that the chemical composition of cast irons may satisfactorily vary over a wide range, it must be remembered that the cast iron entering an enameling shop must not vary over any such range. The coefficient of expansion of the iron is controlled by the composition of the iron, and any variation in the coefficient of expansion will result in crazing and chipping of the enamel. It is possible to vary the composition of the enamel to fit the different cast irons, but a uniform grade is necessary, if the enameling plant is to produce a good quality of ware without loss due to defects.

The Cast Iron Research Committee of the Enamel Division of the American Ceramic Society was financed by interested manufacturers in the study of the blistering of enamels on cast iron. This work was started at the Bureau of Standards but later turned over to E. P. Poste, who carried it toward completion. The results of this work as reported by Poste ² are as follows:

(1) Irons relatively low in silicon and high in combined carbon, especially those that are not readily annealed by the heat treatment incidental to enameling, are more prone to blister than those of the reverse nature.

(2) Blistering is apparently associated with the presence of certain carbon compounds at or near the surface of the iron. In extreme cases the conditions promoting blistering are so generally distributed throughout the casting as to be effective after the surface layer has been removed.

² E. P. Poste, The Blistering of Cast Iron Enamels. J. Am. Ceram. Soc. 16, 227 (1932).

(3) Metallographic evidence has indicated that, in the case of badly blistering irons at least, free carbides are pronounced in the iron, and analytical data support this observation.

(4) Carbon dioxide evolution is in general more copious with nonblistering than with blistering irons when they are heated exposed to air.

(5) From iron coated with enamel, carbon dioxide evolution practically ceases when the enamel reaches a temperature sufficient to cause fusion.

(6) Heating both types of iron in nitrogen results in essentially no carbon dioxide formation.

(7) Blistering iron when coated with enamel and heated in an atmosphere of nitrogen fails to blister.

(8) The last three statements indicate that oxygen from the air is necessary for the formation of carbon dioxide and blistering.

(9) These several observations point to a probable reaction between carbon in the metal and oxygen as related to blistering.

(10) Certain special cases offer analytical and metallographic evidence to indicate that the presence of iron oxide, generally distributed or segregated, may be a cause of blistering.

(11) The behavior of thin applications of enamel to hot castings of blistering iron has suggested a possible reaction between blistering iron and enamel, termed the Manson effect.

(12) Combinations of iron and enamel which have caused blistering and have shown the Manson effect have also developed superior adherence.

(13) An effort to account for these facts in terms of a possible reaction between blistering iron and metallic oxides in enamel produced negative results.

(14) No evidence has been noted that would suggest the enamel itself as the source of gas causing blistering.

(15) No work has been done to determine a possible relation between blistering and gases other than oxides of carbon.

(16) The most logical statement in view of present knowledge is that (*a*) a reaction between oxygen in the air (or iron oxide within the castings in special cases) and certain forms of carbon in the iron produces carbon oxide gases which cause blistering; (*b*) that some irons are free from harmful amounts of this particular form of carbon, others contain it in a concentrated amount at the surface only, while in extreme cases it exists throughout the castings; (*c*) that the total amount of carbon oxide gases evolved at temperatures incidental to enameling is not related to blistering, but that minute amounts at certain critical periods which have escaped detection by the methods employed may be responsible for blistering; and (*d*) that coincident with these conditions is a reaction which promotes adherence of enamel to the iron.

These statements definitely indicate the type of iron most desirable for enameling which, in view of all the facts at hand, may be given as follows:

<i>Constituent</i>	<i>Per cent</i>
Silicon	2.60
Sulphur	Not over 0.080
Phosphorus	Varying with type of pig iron used
Manganese	0.50-0.60
Total carbon	Not over 3.40

These figures and good foundry practice should produce iron free from blistering of the type under investigation, and are based on the kind of castings usually involved in stove foundry practice. Changes in silicon content with corresponding differences in total carbon would be indicated for castings of other types.

DESIGN OF THE CASTINGS FOR THE ENAMELING

Properly designed castings are essential to successful enameling of cast iron by either the wet or the dry process. The casting should have well rounded corners and edges, both inside and out, for the enamel tends to chip or craze and does not cover well in such places. There is a tendency for the enamel to flow away from these sharp edges, with the appearance of a dark line where the enamel is thin.

Castings to be enameled should be so designed as to heat uniformly in the enameling furnace. If this is not done, the enamel on the parts which heat more rapidly will be properly fired sooner than the other parts, or they will be fired too hard when the rest of the enamel is properly fired. Such a condition leads to defects in the enamel and an unsatisfactory appearance. The design of the casting to facilitate uniform heating in the enameling furnace requires experience, since the rule of keeping the casting of uniform thickness does not always apply. Any projections or even edges of the castings tend to heat first. The backs of wash basins, for example, heat faster than the bowls, and must be slightly thicker in the well-designed casting. Lugs and protruding parts should be kept at a minimum, because they heat first and retard the heating of the adjacent metal. Castings, that are not properly designed, often crack or warp in the enamel firing operation. Although it is possible to enamel castings which are not properly designed, it is so difficult and costly that the design should receive careful attention. Co-operation between the enameler and the designer or pattern maker is essential.

FOUNDRY PRACTICE

The making of castings to be enameled is in general the same as ordinary foundry practice. The iron is melted in cupolas and conveyed to the sand molds in ladles. The patterns are usually made of metal and are especially designed to aid the enameling operation. The molds are made either by hand or by machine, the latter being the more common with large production. Molds for large sized castings, such as bath tubs, are all made by machine. The drag and cope are each made on separate machines, the parting line being at the rim of the tub, or at the rim and the bottom of the apron. Sand slingers are used to fill the molds, and cranes and conveyors are employed for handling.

Facing materials are often injurious to castings to be enameled and, if possible, are avoided entirely. Organic material in the facings tends to deposit carbon in the pores of the iron, producing blisters in the enamel. All castings have a thin, hard skin on the surface, which should be avoided as much as possible in making enamel castings. A casting should have a smooth, clean, fine-grained surface, free from dirt, slag, and sand holes. They are usually cast with the side to be enameled down, so that any dirt in the mold will float toward the back side of the casting.

The gates should be on the edge and never on the face of the casting. They should be as liberal as possible, at least two being used for large castings so that the iron can be poured quickly. Skimmer gates are sometimes necessary and should be used whenever there is much danger of slag and dirt being trapped in the casting. The sand used should be as open as practicable, the water content not exceeding about seven per cent.

The cores used in making castings are made with many different bonding materials. Drying and semi-drying vegetable oils such as wood, linseed, corn, and soy bean oil, water plastic gluten, dextrin, glutrin, flour, natural resins, pitches, and alkyl resins are used. Many difficulties are involved as the requirements are quite rigid. Ready workability, the ability to be hardened during baking, mechanical strength, permeability, heat resistance, production of a smooth surface, and the ready disintegration after the casting has been poured, are required.

In pouring the castings, the metal should be hot and, if practicable, that from the middle of the heat only is used for enamel castings. If the iron is too hot, however, it tends to burn into the sand and form a hard, tough skin on the casting, which is difficult to remove with a sand blast. Castings to be enameled should not be kept in the molds longer than necessary, as they tend to absorb water from the sand.

In making the cast iron for enameling, only first class materials should be used, as a high percentage of dirt may be introduced into the iron by foreign scrap. A good grade of pig iron should be used and the scrap should be carefully selected. Chemical analyses are important in the compounding of the batch and are utilized by most of the larger and more modern foundries.

The cupola in which the iron is melted is a vertical cylindrical furnace, into which fuel, flux, and iron are charged. The burning fuel melts the iron and the flux slags the ash and impurities. Figure 35 shows a vertical section of a typical cupola. It consists of a boiler plate

shell three-sixteenths to three-eighths inches thick with a lining of eight to twelve inches of refractory brick or cupola blocks. The size is ordi-

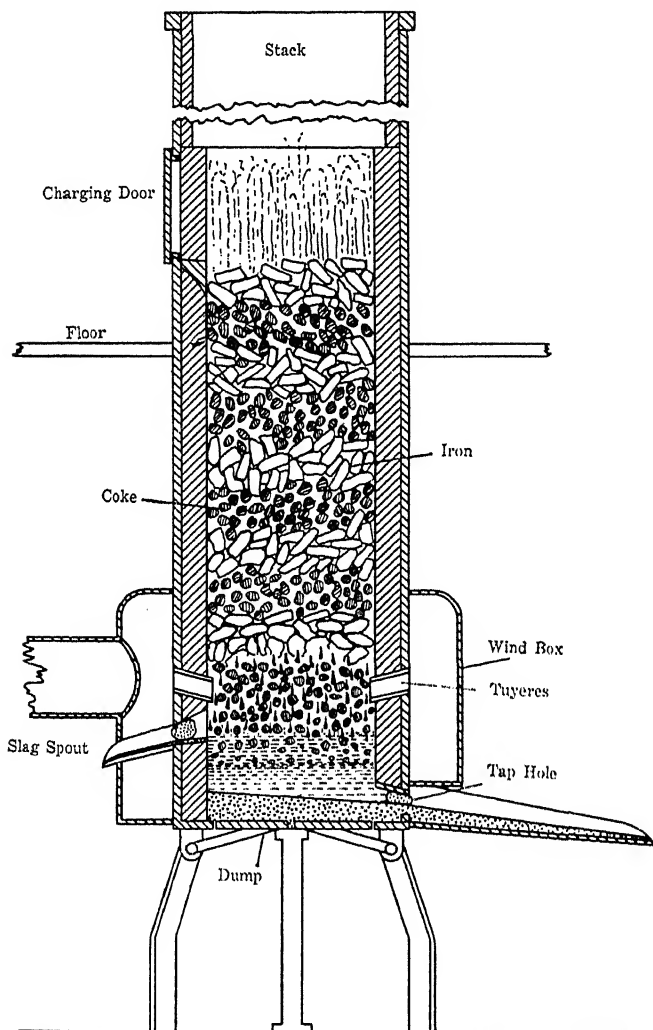


FIGURE 35. A Cast Iron Cupola.

narily indicated by the inside diameter, varying in ordinary practice from sixteen to eighty-four inches. The height is generally given as the distance from the bottom plate to the charging door, the height of the stack varying with the size of the cupola. The ordinary cupola is about

fifteen feet high, but the continuous type may be much higher than this.

The cupola is charged through the charging door, the fuel and iron being added intermittently so that they form a series of layers, as shown in the diagram. Because of the compact nature of this charge, it is not possible to operate the cupola on natural draft alone, and forced draft must be used. A sheet iron chamber, called a wind box, entirely encircling the lower part of the furnace, is used to distribute air under pressure to the different tuyeres at the base of the combustion chamber, but above the slag spout. A slag spout is used to tap the slag off the surface of the metal prior to pouring. A tap hole and spout are built on a level with the floor of the cupola. Cupolas are always built above the floor or over a pit so that at the end of a run the bottom of the cupola, which is built as two large doors lined with refractory, is opened and the dump falls out, being quenched in water. Before operating the cupola again, the slag is chipped off of the refractory and the bottom doors are again shut and cemented in place with fire sand.

Operation. Although there are no set rules for the successful operation of the cupola, the procedure is, in general, about as follows: the bottom doors of the cupola are propped shut and the bottom of the cupola is sealed with clay and sand. This bottom should be so built that the metal will drain through the tap hole, and it must be made of materials which will not fuse too hard to permit the dumping of the cupola at the end of the operation.

The bottom of the furnace is charged with oily waste, shavings, and kindling, over which the bed of coke is laid. The coke is filled up to about two feet above the tuyere and the fire started through the breast opening. Natural draft only is used, the air entering the peep holes over the tuyeres, and the breast opening. As the fire gets up into the coke, the breast opening is closed with fire clay, leaving a small tap hole in line with the floor of the cupola. The spout is lined with fire clay and smoothed off so as to drain easily. The spread of the fire through the coke bed should be uniform and should proceed to the top of the bed in one to three hours. The bed charge of iron is then added, one to four pounds of iron being used to one pound of coke. This bed charge of iron and the succeeding charges of coke and iron should be put into the cupola as soon as the coke bed is burned through. When the charges have been made up to the bottom of the charging door, it is closed and the iron is allowed to soak in the heat of the furnace for about one-half hour. By this time the clay in the breast opening should

be dry, whereupon the peep holes are closed and the air blast is turned on.

In about ten minutes more the metal should begin to run out of the tap hole. The first fifteen to twenty-five pounds will be too cold for casting and should be discarded. The tap hole is then closed and the hot molten iron allowed to accumulate.

Long iron bars are used for tapping the melt, care being exercised so as not to cause a sudden rush of iron. The iron should run out in a smooth stream and when enough has been obtained, the tap hole is again closed with a conical clay bot stuck to the end of a stopping bar. A stopping bar is a straight rod with a disk on the end, which forces the clay into the tap hole. A clay bot is made of a refractory plastic clay and about twice its weight of molding sand.

The metal is conveyed from the cupola to the molds in ladles, which are sheet iron shells lined with refractory clay. The scum floating on the top of the metal is skimmed off with a rod called a skimmer, and the molten metal is poured into the sand molds. The temperature of the metal must be right for pouring the kind of casting to be made. A thin light casting requires rapid pouring of hot metal, but a large heavy casting should be poured with a cooler metal. Hot metal in large castings fuses the sand and produces too great a shrinkage of the casting. A mold must be filled without stopping or the casting will be defective.

Having used all of the iron desired or having melted all of the iron in the cupola, the excess is drawn off and cast into pigs. The blast is then shut off, the tuyere peep holes opened, and the props under the bottom doors removed. The residue which falls out of the bottom of the cupola is sprayed with water and any coke or iron saved for another heat.

There are many problems involved in the operation of a cupola, e.g., the life of the refractory, the costs of fuel, the impurities in the fuel, the most efficient operation, and the demand for the different types of castings, being only a few of the many factors which must be considered.

Cleaning the Castings. After the castings have been shaken out of the molds and cooled, the fins, sprues, and other projections are broken or ground off. Small castings are tumbled or rattled in a cylindrical rotating mill with small pieces of cast iron and sometimes sand. If this process is carried on too long, the surfaces become peened. This interferes with the sand blasting and cleaning of the iron. Chemicals are not usually used in the rattling of castings to be enameled. After

the rattling operation the castings are dressed with grinding wheels, all projections, slivers, and lumps being ground down smooth.

A coarse sand blast is used to remove the molding sand from large castings, such as bath tubs and other sanitary ware, which can not be rattled. This leaves the casting only partially clean, in which condition the projections are ground off with grinding wheels. It is in this condition that the castings are usually sent to the enameling shop, where they receive their final blasting and inspection before being enameled.

CHEMISTRY OF SHEET IRON AND STEEL

The selection of a good base of sheet iron or steel is essential to successful enameling. Two types of sheets are used, sheet iron enameling stock and enameling steel. Typical compositions of these stocks are shown in Table 9.

TABLE 9
TYPICAL COMPOSITIONS FOR ENAMELING SHEETS

	<i>I</i> <i>Enameling</i> <i>Iron</i>	<i>II</i> <i>Enameling</i> <i>Steel</i>	<i>III</i> <i>Enameling</i> <i>Steel</i>	<i>IV</i> <i>Ordinary</i> <i>Steel</i>
Carbon.....	0.013	0.05	0.14	0.20
Silicon.....	trace	trace	trace	0.02
Sulphur.....	0.02	0.035	0.043	0.05
Phosphorus.....	0.0075	0.005	0.036	0.04
Manganese.....	0.023	0.30	0.450	0.40

Number I represents enameling iron which is very low in carbon and impurities. It is the best stock from the enameling standpoint, as there is less tendency for blisters, fishscale, and boiling from this metal than from the steels. It is used chiefly for table tops, refrigerator linings, signs, and other large ware because of its advantage of producing fewer defects in the enamel.

Numbers II and III represent the compositions of good enameling steels used for some types of enamel ware. Enameling steels are somewhat cheaper than enameling irons because of the longer period required to refine the latter in the open hearth, and the more rigid inspection which it usually receives.

Number IV is an ordinary steel which can be enameled, but which shows a greater tendency toward enameling defects than the other three. It is a cheaper steel, but is not commonly used for enameling unless greater strength is required. Steels can be enameled with carbon contents as high as 0.50 per cent, if the silicon is low, but the higher

percentages tend to produce numerous blisters. The steels containing the higher carbon contents can best be used with soft enamels, for the higher the temperature the greater the tendency toward blistering. If silicon is present, it may be counteracted by the presence of manganese, but an excessive amount of the latter induces crazing. High silicon steels are to be avoided, silicon never being allowed to exceed 0.2 per cent. The amounts of sulphur and phosphorus occurring in commercial steels do not seem to affect the tendency for the enamel to blister. Many irons and steels contain non-metallic inclusions of alumina, ferrous oxide, and manganese sulphide, but these constituents do not produce blistering. Small amounts of chromium, nickel, vanadium, molybdenum, and cobalt do not cause the blistering of the enamel, but nitrides do have this definite tendency.

Warpage of enameled sheets is much more common with steels than with the pure iron. This, however, may be due to other causes, such as the thermal expansion of the enamel, irregular heating and cooling, and the method of supporting the ware.

The sheets of enameling iron, some as wide as seventy-two inches, come to the shop in large stacks. These sheets are cut to size to form blanks and are then fabricated.

For the small cheap kitchen ware, thirty-one gauge stock is used, while for larger ware, twenty-four to twenty-eight gauge is necessary. The heavy gauge iron makes a much more durable product and is the basis of chip-resisting enameled kitchen ware. It is possible to strike an enameled surface a severe blow with a blunt instrument, if the metal back of it is sufficiently rigid to resist deformation. Stove parts, small signs, and specialties use twenty to twenty-four gauge sheets. Eighteen to twenty gauge stock is used for table tops, refrigerator linings, and signs. Washing machine tubs and signs are made from sixteen to eighteen gauge stock, and for heavy ware such as chemical or food tanks as high as four to ten gauge, may be required. Table 10 gives the gauges for sheet metal. The physical appearance of enameling sheets is a smooth velvety surface, not spongy, but firm and fine-grained.

Forming. The forming of enameling shapes is usually done by cutting, punching, stamping, drawing, and spinning. The first operation in forming the ware is that of *blanking*, which is cutting or stamping out a piece of the sheet which contains just enough metal for shaping the ware. In this operation the sheet is usually laid out so that the minimum amount of scrap is formed. *Punching* is an operation in which the holes are punched in the sheet. Too many sheets should not be punched at one time or ragged edges will be produced. *Drawing* is

the operation of cupping the sheet as a step in the formation of the final shape. Usually several drawing operations are required to obtain deep shapes, sometimes involving intermediate annealing operations. The steel will withstand a certain amount of stretching without tearing, but beyond this point an annealing operation is necessary to relieve

TABLE 10
WEIGHT AND APPROXIMATE THICKNESS OF SHEET STEEL
United States Standard Gauge for Sheet and Plate Steel

<i>Number of Gauge</i>	<i>Weight per square foot in pounds Avoirdupois</i>	<i>Equivalent thickness of steel in decimal parts of an inch</i>	<i>Approximate thickness in fractions of an inch</i>
0000000	20.0	.4900	$\frac{1}{2}$
000000	18.75	.4594	$15\frac{3}{32}$
00000	17.50	.4288	$\frac{7}{16}$
0000	16.25	.3981	$13\frac{3}{32}$
000	15.00	.3675	$\frac{3}{8}$
00	13.75	.3369	$11\frac{3}{32}$
0	12.50	.3063	$\frac{5}{16}$
1	11.25	.2757	$\frac{9}{32}$
2	10.625	.2604	$17\frac{1}{64}$
3	10.0	.2451	$\frac{1}{4}$
4	9.375	.2298	$15\frac{3}{64}$
5	8.75	.2145	$\frac{7}{32}$
6	8.125	.1991	$13\frac{1}{64}$
7	7.50	.1838	$\frac{3}{16}$
8	6.875	.1685	$11\frac{1}{64}$
9	6.25	.1532	$\frac{5}{32}$
10	5.625	.1379	$\frac{9}{64}$
11	5.0	.1225	$\frac{1}{8}$
12	4.375	.1072	$\frac{7}{64}$
13	3.75	.0919	$\frac{3}{32}$
14	3.125	.0766	$\frac{5}{64}$
15	2.1825	.0689	$9\frac{1}{128}$
16	2.50	.0613	$\frac{1}{16}$
17	2.25	.0551	$9\frac{1}{160}$
18	2.00	.0490	$\frac{1}{20}$
19	1.75	.0429	$7\frac{1}{160}$
20	1.50	.0368	$\frac{3}{80}$
21	1.375	.0337	$11\frac{1}{320}$
22	1.25	.0306	$\frac{1}{32}$
23	1.125	.0276	$9\frac{3}{320}$
24	1.00	.0245	$\frac{1}{40}$
25	.875	.0214	$7\frac{3}{320}$
26	.75	.0184	$3\frac{1}{160}$
27	.6875	.0169	$11\frac{1}{640}$
28	.625	.0153	$\frac{1}{64}$
29	.5625	.0138	$9\frac{1}{640}$
30	.50	.0123	$\frac{1}{80}$

the strains in the metal and prevent its rupture on further drawing. With the development of better drawing stock and methods, it is now quite common to draw washing machine tubs without intermediate annealing operations. *Spinning* is an operation of rotating the drawn piece or the blank on a lathe and then forcing the metal to flow by means of rollers pressed against the rotating metal. It is of especial advantage in making shapes like coffee pots, which have an opening smaller than the maximum diameter of the vessel. It is not possible to draw such shapes.

Beading is the turning of a bead on the rim of the ware by rotating it and holding the edge in a set of rollers. These operations are all fairly simple, but difficulties are often encountered in the making of a new shape or a change of the metal stock. The oils used must be of the soluble type to facilitate their removal before the enamel is applied.

Welding can be done either by the electric or the oxy-acetylene method. If the oxy-acetylene method is used, a neutral flame should be employed and, if the metal is to be enameled on only one side, it should be welded on the other. If it is to be enameled on both sides, the weld should be slightly built up to permit a grinding away of the surface where the fluxes always tend to collect. The weld rod should be of metal similar to that of the base metal stock.

Electric welding may be done by either the arc or spot weld method. The former is used for heavy stock and makes a very satisfactory weld if annealed. The latter is more common, since it has been applied to machines whereby the spot welder acts as a stitch welder in making a series of spots so close together that they touch. These welds are very satisfactory for enameling. The spot weld is used quite extensively on thin stock and for welding lugs in place.

CHAPTER 5

Preparation of the Metal Surfaces for Enameling

The metal shapes delivered to the enameling shop must be cleaned and prepared for the application of the enamel, as the quality of the finished ware depends greatly upon the character of the metal surface. Such defects as blisters, chips, poor adherence, and fishscale can be traced to this cause and much of the trouble encountered in enameling is related to it. There is probably no operation so easily slighted and requiring more rigid inspection than the preparation of the metal for enameling. It is the step in the process where many of the defects can be prevented before considerable expense has been put into the ware. If ware shows defects after the enameling has been completed, the cost of de-enameling and re-enameling is often so great that the ware cannot be economically reworked.

The cutting, stamping, drawing, and spinning operations on sheet steel leave the metal coated with oil and during storage and transportation the surface often becomes dirty and rusty. This oil, dirt, and rust must be removed before the enamel is applied.

Castings come from the foundry partially coated either with a thin scale and foundry sand or with the surfaces peened from the tumbling process. Mold marks, sharp edges, and fins must be ground off with grinding wheels and the surface cleaned thoroughly. Cast iron is practically always blasted clean with sand or steel grit, which leaves a slightly roughened surface most suitable for enameling.

SHEET IRON AND STEEL METHODS

The preparation of sheet metal surfaces for enameling varies with different types of ware, but the object is the same in all methods. The oil, deposited on the shapes during forming, the rust, and the scale must be removed, leaving a smooth but not polished surface.

Methods. The oil can be removed from the surface by annealing, by sealing, or by means of a chemical cleaning solution. Organic solvents, such as gasoline, are seldom used because of the fire hazard, the cost, and the thin film which is usually left on the ware.

Annealing is a heating operation, following the shaping of the iron, to remove any strains in the metal, and, since the metal is heated to redness, the oil is burned off. Most ware does not require an annealing operation; therefore it is not as common as the other methods.

Scaling consists of heating the stock in the presence of acid or sulphur fumes, primarily to clean the ware, although annealing is a secondary function. An oxide scale is, thereby, formed on the surface of the metal, the scale and dirt being consequently removed together in the pickling operation which follows.

Chemical cleaning is a washing operation to remove oil and dirt from the surface of the ware. The chemical cleaner is an alkali and soap solution, the alkali saponifying the soluble oils and the soap aiding in the emulsification of the oils and the removal of the dirt.

Pickling is an operation in which acid solutions are used to remove rust and scale from the metal surface. The pickle solutions, which are sulphuric or hydrochloric (muriatic) acid, attack the rust and the iron under the scale. The formation of hydrogen gas at the metal surface loosens the scale, forcing it from the iron. The metal surface becomes slightly roughened because of the selective solution of the iron and the surface is left in a suitable condition for enameling.

Sheet metal is *sand blasted* when large pieces of heavy gauge stock are used. Sand blasting is not common, however, as most sheet iron is warped by the force of the sandblast.

ANNEALING

Annealing serves two purposes in enameling: (a) it removes strains in the metal; (b) it burns any adhering oil from the piece. It is commonly employed for sheet metal shapes which have been stamped or spun, but sometimes it is used for cast iron shapes. The temperature of annealing may vary with the thickness of the ware and the time allowed, but is generally red heat (1150 to 1400° F). The grease should be completely burned from the ware, which is evidenced by the cessation of flames and fumes, the metal reaching a cherry-red heat. Five to ten minutes are generally required for this operation.

The metal should be stacked so that all surfaces are exposed to the furnace atmosphere, resulting in a complete oxidation of the oil and carbon. If the ware is annealed at too high a temperature the scale is fused to the metal and is very difficult to remove in pickling.

SCALING

Scaling is closely related to annealing, but the object is in some respects different. In scaling it is desired to form a soft scale of oxide all over the ware. This forms readily if the furnace atmosphere contains acid or sulphur fumes. It is common to scale in a continuous furnace, the acid being sprayed on the ware as it passes into the hot chamber. In such cases the ware travels on a chain conveyor through a tunnel over the hot zone. If sulphur is used in the scaling furnace, one should be cautious, as a very small percentage of sulphur accidentally contaminating the atmosphere of an enameling furnace will produce pitting and scum. It is better not to burn sulphur in the vicinity of an enameling furnace. Waste pickle acid is often used as the source of acid for the scaling operation. Scaling is used chiefly where annealing is necessary, but compared with chemical cleaning it is relatively expensive.

THEORY OF CHEMICAL CLEANING

The chemical cleaners are alkaline solutions containing colloidal material, which depend for their action upon the phenomena of saponification and emulsification.

Saponification is the chemical reaction between the alkali of the cleaner and the fatty acid of the oil to form a soap and glycerine. The soap formed in the cleaner solution is soluble and can, therefore, be readily rinsed from the ware.

Emulsification is the phenomenon of bringing one liquid into suspension as minute droplets in another liquid. The oil as well as the dirt from the iron is suspended in the cleaner solution by this reaction.

Saponification and emulsification work together in the cleaning operation. The alkali not only promotes the saponification but it also influences the emulsification. Likewise, the resulting soap lowers the surface tension, bringing about emulsification, and by doing this it presents a greatly increased oil surface to the alkali, thereby aiding in the saponification.

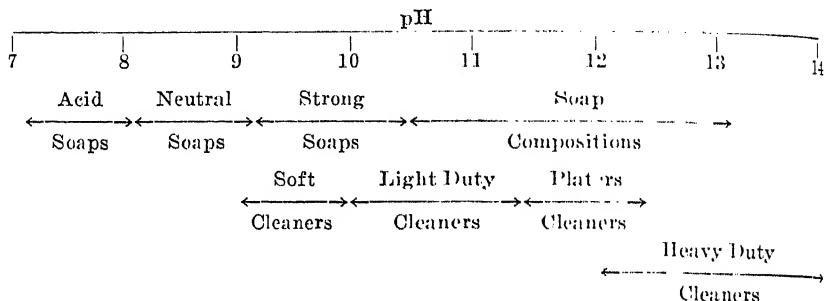
The ionization of the alkali present in the cleaner solution is of primary importance, for it is only the ionized alkali that is active. Figure 36 shows the range of the hydrogen ion concentration (pH value)* of the typical industrial cleaner solutions.

The hydrogen ion concentration of cleaner solutions depends on both the amount and the kind of alkali used. The pH value of a solu-

* The pH value is the negative log of the hydrogen ion concentration. It indicates the acidity or alkalinity of a solution.

tion does not generally increase in proportion to the concentration. This is because only a part of the alkali ionizes, some remaining in solution in the molecular condition. For example, sodium hydroxide

FIGURE 36.
ALKALINITY RANGE OF INDUSTRIAL CLEANERS (pH VALUE)¹



ionizes in water as follows: $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$. The reaction is reversible and both molecular and ionized sodium hydroxide are present. Figure 37 shows the pH values of a number of compounds at varying concentrations.

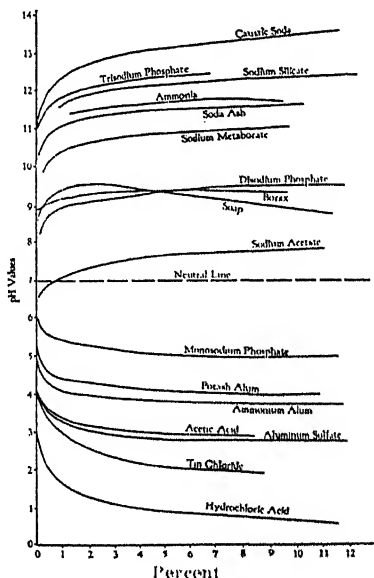


FIGURE 37. Alkalinity and Acidity (pH Value) of Different Compounds at a Given Temperature.²

¹ R. W. Mitchell, *The Cleaning of Metal, Metal Cleaning and Finishing*, Jan. 1930.

² *Ibid.*

Ionization increases with an increase in temperature, which accounts for the greater chemical activity of many solutions when heated.

The diagram in Figure 38 shows the relation between the pH value, the degree of ionization, and the concentration of sodium hydroxide solutions at a temperature of 70° F. The per cent ionization is decreased with the increase in concentration while the pH value is increased quite rapidly at first and then remains nearly constant.

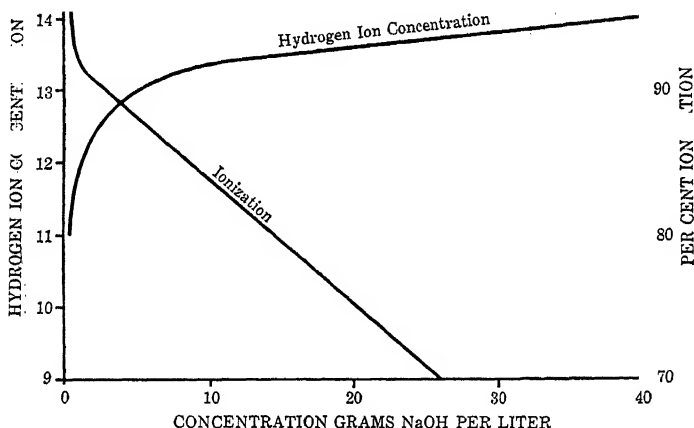
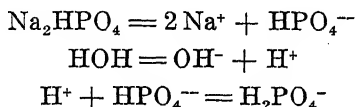


FIGURE 38. Ionization of Sodium Hydroxide.

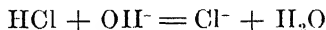
The fact that different materials ionize to different degrees is taken advantage of in the making of cleaners. Salts which have this property to a marked degree form what are called *buffer solutions*. In such solutions the ions that are removed by chemical reaction are constantly replaced by the further ionization of the reserve portion of the salt. The pH value is, therefore, kept constant even when the ions formed are being constantly consumed by the action of the solution. For example, the salt, disodium phosphate, is used in cleaners to form a buffer solution. The reaction is illustrated by the following equations:



Added NaOH is absorbed thus:



Added HCl is absorbed thus:



and by hydrolysis of the Na_2HPO_4 , OH^- is again formed to replace that consumed.

The diagram in Figure 39 shows the effect of adding acid and alkali to buffered and non-buffered solutions.

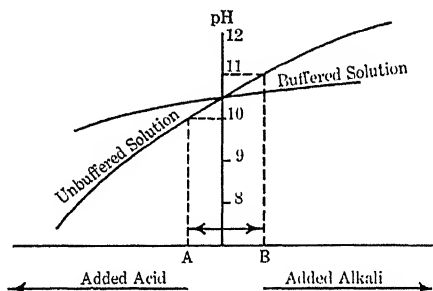


FIGURE 39.
The Effect of Buffer Solutions.³

Given two solutions, one buffered and the other not buffered, with a pH of 10.5, the diagram shows that an addition of A amount of acid to the unbuffered solution lowers the pH to 10, while an addition of a much greater amount is necessary to lower the pH an equivalent amount with a buffered solution.

Likewise, an addition of B amount of alkali raises the unbuffered solution to a pH of 11, while a much larger amount is required to raise the pH of the buffered solution an equivalent amount.

Cleaner solutions are all buffered solutions, since it is desirable to keep the pH value as constant as possible. The materials commonly available for cleaner solutions are shown in Table 11.

When any material has a state of subdivision giving particle sizes between one millimicron* and one hundred millimicrons in diameter, it is considered to be in the colloidal state. All cleaning solutions contain colloids as finely divided suspensions or emulsions. The col-

* *Ibid.*

* A micron is one thousandth of a millimeter, and a millimicron is one thousandth of a micron or one millionth of a millimeter.

loids commonly used in cleaner solutions are listed in Table 12. Although these materials are used for their colloidal properties, they are mildly alkaline.

TABLE 11

INORGANIC COMPOUNDS USED IN CLEANER SOLUTIONS

Caustic soda.....	NaOH
Caustic potash.....	KOH
Ammonia.....	NH ₄ OH
Sodium carbonate.....	Na ₂ CO ₃
Sodium carbonate (hydrated).....	Na ₂ CO ₃ ·H ₂ O
Sal soda.....	Na ₂ CO ₃ ·10H ₂ O
Sodium bicarbonate.....	NaHCO ₃
Sodium sesquicarbonate.....	NaHCO ₃ ·Na ₂ CO ₃ ·2 H ₂ O
Potassium carbonate (also hydrates).....	K ₂ CO ₃
Ammonium carbonate.....	(NH ₄) ₂ CO ₃
Disodium phosphate.....	Na ₂ HPO ₄ ·12 H ₂ O
Trisodium phosphate.....	Na ₃ PO ₄ ·12 H ₂ O
Sodium tetraborate (borax).....	Na ₂ B ₄ O ₇ ·10 H ₂ O
Sodium metaborate.....	NaBO ₂ ·2 H ₂ O
Sodium aluminate.....	NaAlO ₂
Sodium cyanide.....	NaCN
Sodium silicates.....	Na ₂ O·SiO ₂ to 4 Na ₂ O·SiO ₂
Sodium metasilicate.....	Na ₂ O·SiO ₂ ·5 H ₂ O
Sodium potassium carbonate.....	NaKCO ₃ ·6 H ₂ O

TABLE 12

COLLOIDAL MATERIALS USED IN CLEANER SOLUTIONS

Sodium oleate	Sodium stearate	Rosin soaps
Potassium oleate	Potassium stearate	Sulphonated oil
Ammonium oleate	Ammonium stearate	Pectic acid
Sodium linoleate	Sodium palmitate	Starch
Potassium linoleate	Potassium palmitate	Gums
Ammonium linoleate	Ammonium palmitate	Amino acids
		Clays

The soaps function in the cleaner by lowering the surface tension of the solution, thereby bringing about the emulsification. Figure 40 shows the effect of soap on the surface tension of water at 23° C. Note that the surface tension drops nearly to a minimum with the first 0.1 per cent addition of soap.

According to the present theory of the action of the soap in emulsification, the soap acts as a sort of introducer between the water and the oil. The soap molecule is soluble in the oil at one end and

The soaps used for cleaning are limited to the sodium, potassium, or ammonium compounds, as these are the only ones soluble in water. The ammonium soaps are, however, not stable and are seldom used. The fatty acid end of the soap may be any of a great variety of vegetable or animal oils or greases and has a profound effect on the properties of the soap, influencing its ability to emulsify the oil, its solubility, and its rate of activity. A satisfactory soap must have good rinsing properties and must not become curdy or sticky.

Since soap in the cleaner solution is at least partially formed by saponification of the oil on the ware, the choice of these oils is always a consideration in the cleaning problem.

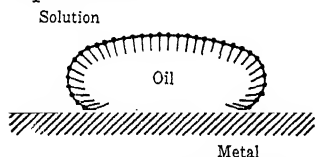


FIGURE 41. Graphic Representation of the Action of the Soap Molecules at the Oil-Water Interface.

The lubricants used in the stamping, drawing, and spinning of metal shapes involve various combinations of oils, fats, and greases. A good lubricant forms a continuous adhering film on the metal, protecting both it and the tools from excessive friction. The abilities of these

oils to form continuous films with good adherence varies greatly with the different oils and with the surface characteristics of the metal. The animal and vegetable oils seem to have a greater film forming capacity than the mineral oils and are more readily removed in the cleaning process.

The cleaning of the metal involving the removal of the oil depends to a considerable extent on the oils and on the nature of their adherence. The phenomena of saponification and emulsification must work together. If the oil is a pure mineral oil, the cleaner solution must have a low interfacial tension to accomplish effective wetting. Emulsification is the more important action in this case as the oil must enter the cleaner by emulsification alone, which is a very slow process, even when the solution is hot and well agitated. There is always a tendency for the emulsion to break when thus formed, producing a layer of oil on the surface of the bath. If this process could be made to operate rapidly and the oily layer could be continuously removed, the operation would be ideal. However, it is slow and uncertain and therefore it is undesirable to use mineral oils alone as lubricants on metals which are to be chemically cleaned.

If saponifiable oils, which are essentially glycerides of the fatty acids, are used alone, they are readily converted into soaps by the alkali cleaners. Since the alkali (sodium ion) used forms soluble soaps the solution of the oil is quite simple. Here again a difficulty

appears, however, as large amounts of soap in the solution result in excessive foaming. A combination of saponifiable and non-saponifiable oils is, therefore, more desirable since it permits both saponification and emulsification to work at maximum efficiency. The oils of either type are emulsified to a certain extent. The surface area is greatly increased by this change and saponification of the fatty oils progresses very rapidly. This results in a lowering of the interfacial tension of the solution because of the additional content of soap, which in turn promotes further emulsification of the oils. The emulsions are more stable and the cleaner works at maximum efficiency.

The removal of the outer layer of the oil film is not very difficult, but it is the removal of the closely adhered layer that requires the most efficient cleaner. The closely adhered oil is believed to be in some sort of a chemical combination with the iron, as an iron soap or iron salt such as iron oleate, which must be broken down by chemical action before it can be removed. It may aid the understanding of the problem to consider that in applying the oil to the iron the greatest possible adherence is desired; hence in removing it, the solution must exert an even greater pull to get it away from the iron. If the lubricants contain metallic soaps, pigments, and drying oils, they may require additional chemical action to free them, but such compounds have no place in enamel practice.

The free rinsing of the cleaner solution from the metal shapes is important, but should not cause difficulty unless insoluble soaps are formed. The rinse should be complete, otherwise the soap will be carried over into the pickling bath, neutralizing it and interfering with good operation.

Since the work accomplished by different cleaners varies, no single composition can be given which will serve all purposes. The method of operation, the nature of the dirt or oil to be removed, and even the nature of the ware to be cleaned, influence the choice of cleaners. The methods of testing the cleaner solution are given on page 101.

ELECTROLYTIC CLEANING

Electrolytic cleaning is similar to the regular chemical cleaning, except that the reactions are accelerated by the flow of an electric current through the bath. The ware is generally made the cathode and the metal tank the anode, although in special cases this is reversed.

The alkali content of the bath should be five or six ounces to the gallon with a pH value of about twelve. This gives the bath good electrical conductivity which is necessary to avoid a high voltage.

drop through the solution. Six to twelve volts are generally employed with a current density of about ten amperes per square foot on the ware. Too low or too high a current density slows down the operation. If the current density is too low, the activity is sluggish; and if the current density is too high, the violent gas evolution produces a film over the ware, which develops a resistance to the current flow. In electrolytic cleaning the soap content of the solution should not be over one fourth of a per cent or it will cause sliming. Chlorides, sulphates, and heavy metal hydroxides should be avoided as they corrode the anode tank. The solution is usually hot, but agitation is derived entirely from the minute bubbles at the surface of the ware. It is the mechanical action of these bubbles in throwing the grease and oil into the emulsion that greatly accelerates the electric cleaning operation. In addition, however, the alkali content is increased at the cathode which thereby accelerates its activity.

Electrolytic cleaning is much more rapid than still cleaning and is, therefore, becoming more common, especially where continuous automatic cleaning equipment is being used.

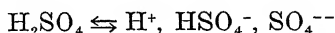
THEORY OF PICKLING

To remove rust and scale from the metal ware it is pickled in an acid solution. The acid dissolves the rust and attacks the iron, liberating hydrogen gas which forces the scale from the surface. The most important part of the pickling process is the removal of this scale from the metal. Most of it falls to the bottom of the tank forming a sludge. Three different oxides may be present on the iron to be pickled: hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), anhydrous ferric oxide (Fe_2O_3), and magnetic iron oxide (Fe_3O_4). The first type ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is ordinary water rust and is quite soluble in the pickle acid. The second type (Fe_2O_3) is the hard brown rust formed on long standing. Much of this rust is dissolved in the pickle solution, but some settles to the bottom of the tank. The magnetic iron oxide is the high temperature form, or black scale. It dissolves only very slowly and makes up most of the sludge in the bottom of the tank.

The pickle solution usually consists of about six per cent sulphuric acid, or about eleven per cent of hydrochloric acid, with water and an inhibitor. In rare cases hydrofluoric acid, and also nitre cake (sodium acid sulphate) are used.

The rate of the attack of the acid on the iron is determined to a great extent by the hydrogen ion concentration of the solution, which depends upon the kind of acid, the temperature, the presence of com-

mon ions, and to the concentration of the acid in the solution. Sulphuric acid ionizes only to a limited extent as follows:



Sulphuric acid is, therefore, in solution as molecular sulphuric acid, H_2SO_4 , and the ions, H^+ , HSO_4^- , and SO_4^{--} . The molecular sulphuric acid acts as a reserve, furnishing new ions as the hydrogen ions in solution are removed by reaction with the iron or iron oxides. The amount of ionization is dependent (other things being constant) on the H^+ ions and the SO_4^{--} ions present in the solution. The addition of SO_4^{--} ions in the form of a salt such as ferrous sulphate for example depresses the ionization of the sulphuric acid. This is caused by the fact that the ferrous sulphate ionizes readily into Fe^{++} and SO_4^{--} ions, thus building up an ion common with one of those, SO_4^{--} , of the sulphuric acid. This phenomenon is called *common ion effect*. Since ferrous sulphate is formed in the pickling operation it accumulates with the use of the pickle bath and finally reaches a concentration where it depresses the ionization of the acid to such an extent that the solution must be discarded.

A concentrated solution of sulphuric acid ionizes only to a slight extent and, therefore, attacks iron only very slowly. A dilute solution, however, ionizes much more and attacks iron more rapidly. The curves in Figure 42 show the hydrogen ion concentration of sulphuric acid and the per cent active acid present for different concentrations. It is apparent that the maximum hydrogen ion concentration for sulphuric acid is obtained when the acid strength is about twenty-two per cent.

This, therefore, is the concentration representing the most active strength and fastest rate of pickling with sulphuric acid. In pickling practice, however, such high concentrations are not used because of the excessive fuming of hot acid and the danger of some of the evolved hydrogen being absorbed by the iron. Concentrations of five to eight per cent are much more common.

As the temperature is increased in solutions of sulphuric acid, the hydrogen ion concentration is slightly decreased, but the increase in the mobility compensates for this in pickling practice. At room temperatures sulphuric acid solutions are less mobile and the speed (rate of movement) of the ions is very slow. In other words an increase of the temperature lowers the viscosity and the speed of the ions is increased to such an extent that the attack on iron is increased, even though the hydrogen ion concentration is lower. Sulphuric acid

pickle solutions are usually heated to 140-150° F to obtain rapid yet controllable operation. The use of higher concentrations at lower temperatures is not satisfactory because of the reduced ionic mobility which is intensified by increased concentrations.

The use of sulphuric acid, therefore, calls for not only an understanding of the ionization which limits the concentrations of acid and of by-products of the pickle reaction, but also an appreciation of the influence of temperature on the mobility, fuming tendency, and the general activity of the acid.

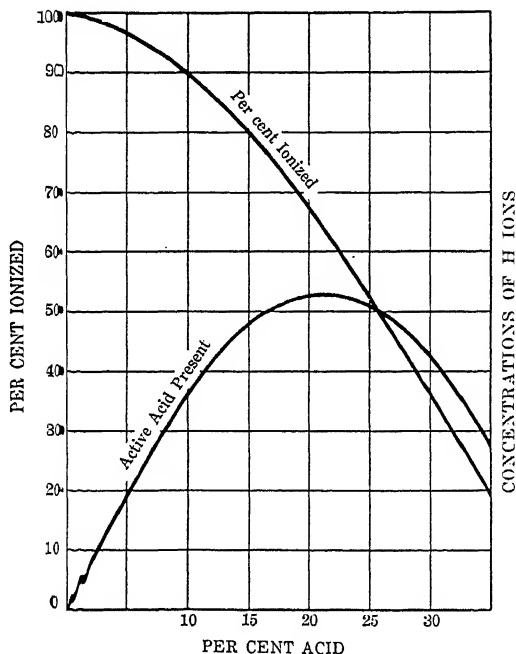
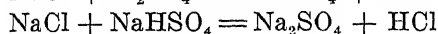
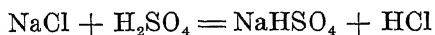


FIGURE 42.
Ionization of Different Strengths of Sulphuric Acid.

Hydrochloric (muriatic) acid differs from sulphuric acid in that it ionizes almost completely even when present in quite high concentrations. It forms very mobile solutions even when cold, does not fume in dilute solutions, and need not be heated. The hydrochloric acid (HCl) ionizes into ions of H^+ and Cl^- . In the pickle reaction the iron is attacked with a formation of $FeCl_2$ and hydrogen gas. The $FeCl_2$ ionizes into Fe^{++} and Cl^- , the Cl^- being a common ion with the Cl^- of the hydrochloric acid. The hydrochloric acid solutions are

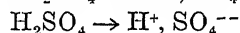
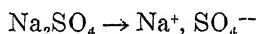
used at room temperature and vary between ten and sixteen per cent in concentration. They are used to a considerable extent in pickling iron for enameling.

The use of salt (NaCl) with the sulphuric acid bath is based on the reaction between salt and sulphuric acid to form hydrochloric acid.



According to the first equation, one molecule of hydrochloric acid is formed from each molecule of sodium chloride, but the reaction in the second equation probably does not contribute much hydrochloric acid as it is very slow at pickling temperatures. In such solutions the combined action of sulphuric acid and hydrochloric acid is obtained in pickling. The rate is intermediate between that for hydrochloric acid and that for sulphuric acid. Sodium chloride added to the sulphuric bath, therefore, increases the rate of pickling because of the accelerated rate obtained by the formation of hydrochloric acid in the solution.

In an attempt to reduce acid expense the by-product, nitre cake, has been used. It is a sodium acid sulphate containing about 65% sodium sulphate and 35% sulphuric acid. It is evident, on considering the ionization of these two constituents,



that the sodium sulphate is a hindrance to the action of the sulphuric acid. The sodium sulphate produces the common ion SO_4^{--} ; therefore, it inhibits the ionization of the sulphuric acid. Where nitre cake is used, high temperatures must be employed to obtain rapid pickling of the iron.

Inhibitors are organic materials such as molasses, starch, spent tanning liquors, rye flour, and sulphite liquor, which reduce the amount of iron dissolved in the pickling operation. Their function is not generally thought to be chemical but rather of a physical or colloidal nature. They probably accomplish two objectives, that of forming a film over the bath, which reduces the amount of fuming of the acid and that of inhibiting the solution of the iron where its cleaned surface is exposed to the solution. This latter effect results in a saving of both acid and metal and it tends to prevent uneven pickling and excessive pitting.

In such colloidal additions there is always present the electrical effect of differently charged particles. The colloidal material in the pickle solution is attracted to the iron freshly exposed by pickling and a thin film of the colloidal material, therefore, forms an enveloping layer which protects these spots from further action. Such conditions, therefore, permit the use of stronger and more rapid pickle solutions. The inhibitor, however, if added in any appreciable amounts, slows down the pickling rate of a given strength of solution. This is probably because of the tendency for the colloidal material to coat the parts of the metal not thoroughly cleaned. It is necessary in the use of inhibitors to strike a balance between the two extremes; one in which no inhibitor is used and where the attack of the metal is encountered, and the other in which the rate of pickling is sacrificed by an excess of the inhibiting action.

ELECTROLYTIC PICKLING

Electrolytic pickling has not met with great favor in the enameling industry. Two different methods are possible, the anode and the cathode process. The less common and less understood is the cathode process in which the iron is made the cathode and an insoluble anode is used. Although sulphuric or hydrochloric acid solutions are used in this process, the entire pickling operation is different from the chemical method. The most common theory of the process is that the sulphuric acid is electrolyzed and hydrogen is deposited on the ware. This hydrogen reduces the oxides of iron and ferrous sulphate is formed. The iron itself is supposed not to be attacked, its solution pressure being supposedly completely stopped by the opposing electromotive force of the electric current.

Anode pickling is similar to the regular chemical process. The ware is made the anode and the tank the cathode. The electric current of low voltage accelerates the pickling action in that it accelerates the speed of the ions. A thin layer of iron is dissolved with the evolution of hydrogen as in the chemical pickling process.

The absorption of hydrogen in pickling is a common phenomenon, especially with steels. The hydrogen evolved in the pickling process is sometimes partially absorbed by the metal sheet, especially where strong acid solutions or rapid pickling are employed. This hydrogen not only affects the properties of the steel, causing a brittleness called acid brittleness, but it causes blistering in the enameling process. An excessive pickling rate should, therefore, be avoided. Staley⁴ recommends a hot water dip to free the iron from the hydrogen absorbed.

⁴ Staley, H. F., Theory of Pickling of Sheet Iron and Steel for Enameling Purposes, J. Am. Ceram. Soc. 9, 787 (1926).

PROCESSES FOR THE PREPARATION OF SHEET METAL SURFACES

The preparation of sheet iron and steel for enameling is subject to considerable variation as shown by the flow sheet in Figure 43. In the smaller enameling plants the work is done by hand and the equipment is limited to a series of tanks containing the various solutions with possibly an overhead crane to transfer the ware in baskets from one tank to another. In the larger, more modern plants the entire operation may be made automatic. A continuous conveyor is used to move the ware in the tanks and transfer it from one to another in a definite time cycle. The concentrations and temperatures of the baths may be automatically controlled and the ware produced in a systematic, uniform, and efficient manner. All variations between these extremes are to be found in different enameling shops, the amount of production, the type of ware, and the economic factors controlling the selection of equipment. In any installation a straight line system should be used.

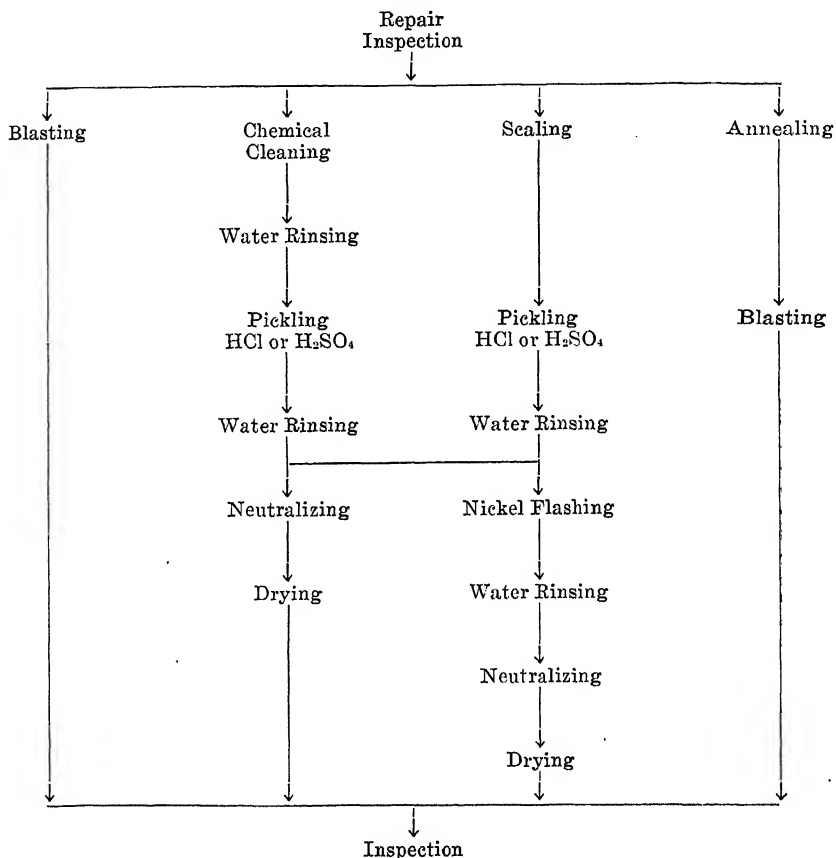
Operations. Before any of the sheet metal parts are sent to the cleaning operations they should be inspected and all defective ware either repaired or discarded. In the repair department, welding, grinding, and straightening equipment should be available. The welds should be inspected for leaks or weaknesses. They should be smoothed down and any projecting fins of metal ground or cut off. Dents should be removed from the ware and it should be inspected for size, warpage, and shape. After passing inspection the ware is ready for the cleaning operations. That to be annealed or scaled is sent to the ovens and that to be chemically cleaned is sent to the cleaning department.

The ware to be scaled or annealed is loaded either on the continuous conveyor passing through the oven or on the charging rack for the intermittent process. The ware must, in either case, be stacked in such a way as to permit a free circulation of air in and around it. This facilitates the rapid burning off of the grease and more uniform heating. The grease on ware that is stacked together tends to carbonize and burn into the iron, making the pickling operation very difficult. The ware that is scaled and annealed is usually taken to a temperature of red heat which rapidly burns it clean. Higher temperatures are objectionable because they cause excessive oxidation and burn the scale into the iron. The ware is then difficult to pickle.

requiring an excessive length of time, and it often becomes pitted. In the scaling operation acid fumes or sulphur are introduced into the furnace. This is usually accomplished by spraying the ware with waste pickle acid as it enters the furnace. The acid vaporizes and

FIGURE 43

Flow Sheet for Preparing the Metal for Enameling



forms a loosely adhering oxide scale over the iron, if not heated to too high a temperature, and in pickling this scale comes off in large flakes.

Sealing is desirable as a cleaning method because it removes all of the dirt, and at the same time anneals the metal. It is objectionable from the standpoint of cost and the equipment required.

Ware to be cleaned chemically is loaded into Monel metal baskets

which carry it through all of the cleaning, pickling, and rinsing operations. It should be packed carefully in these baskets so that the solutions can have access to every part and cover every surface. With pans and similar shapes all chances for entrapping air when immersing the basket in the solutions must be avoided. With sheets, spacers must be used to prevent them from lying flat against one another. Most pieces are placed on edge, but judgment and care must be used.

Monel metal baskets are generally used for these operations as they are resistant to all of the solutions of the cleaning and pickling process. Monel metal is an alloy of copper, nickel, and iron, none of which is objectionable even when dissolved to a slight extent in the solutions.

The basket of ware to be cleaned is first immersed in the boiling alkali cleaner solution, which is agitated by steam or mechanical means. The oil and grease are removed from the ware in a period of from ten to twenty-five minutes, depending upon the many factors already discussed. Any oil or grease rising to the surface of the solution should be skimmed off before removing the ware.

On removal of the ware from the cleaning solution it is allowed to drain into the tank. The solution should run off the ware without the formation of breaks. If the ware is not clean the solution will run off the oily parts first and show an irregular draining called breaking, but if the solution is in good condition and the practice right, breaks should not appear. Ware that shows breaks on draining should be returned to the solution until it is clean.

From the cleaner solution the ware is transferred to the rinse, which is a tank of flowing water. On immersing the basket of ware in the rinse most of the cleaner solution adhering to it will come to the surface of the water. Time is then allowed for this oily scum to pass off the surface and down the overflow. The basket of ware is then raised out of the rinse and, after draining, it is transferred to the pickle bath. Ten to twenty minutes are usually required to dissolve the rust off the iron and to eliminate the scale in the sulphuric acid pickle. A five or seven per cent solution is commonly used and this bath should be at a temperature of 140 to 150° F.

In the hydrochloric acid bath the temperature is usually at about that of the room and the time required is slightly longer than that for sulphuric acid. The concentration of the bath is about eleven per cent.

In either method of pickling, the ware is left in the bath until it is free from rust and scale and then it is withdrawn and momentarily

allowed to drain, after which it is promptly placed in a running water rinse. The excess acid and ferrous sulphate are dissolved by the water and carried off.

On removal from the rinse the ware is momentarily drained and then immersed in the neutralizing bath which is hot (150 to 160° F) and not flowing. In this bath the last traces of acid are neutralized. If the bath is too hot the ware takes on a dark brown color. After neutralizing, the ware is drained and then transferred to a hot dryer with good air circulation, so that the ware will be rapidly dried to avoid the tendency to form an excessive amount of rust. When dry the ware should have a light straw color caused by the thin film of rust which is always present.

The Cleaning Equipment. The room devoted to the preparation of the iron surface for enameling should be isolated from the rest of the plant; it should be well ventilated and well lighted. In many of the older shops this department was placed in some dark corner or shed that could not be used for other purposes. This department, however, because of the fumes and steam which necessarily arise from the baths should be given good ventilation to improve the conditions for the workmen and to reduce the corrosion of the equipment. It should be isolated from the rest of the plant to prevent the fumes entering the plant proper, because of their effect on both the equipment and the ware being processed. The building may be of steel, brick, or wood. All steel and wood parts should be painted with an acid-resisting paint. A paving brick floor is preferable with ample drains and slope to facilitate flushing, which should be frequent. It is best located on the ground floor with plenty of head room for cranes and ventilation. Ample roof ventilators should be provided.

Chemical cleaning tanks are usually made of iron or steel, designed in the most convenient size and shape for the ware being produced. They are heated by either steam coils, steam jets, or hot flue coils. Steam coils are quite common and are used especially where waste steam is available. A vertical metal plate or shield which extends to the ends of the tank, but only to within six inches from the bottom and a few inches below the surface of the bath, is usually installed in front of the coils to aid the circulation of the solution. An overflow and discharge connection is provided. In designing a tank such considerations as size, shape, material, type of ware, discharge, drainage, heating, location, floor loads, cost, and overhead are important.

The steel tanks used may be either riveted or welded, the former being the stronger and the latter the tighter. All pipe joints should

be welded or tightly caulked. The thickness of the metal required depends upon the size of the tank and the tendency toward warping. If ordinary carbon steel is used, rusting is very bad, but some of the rust-resisting steels are quite suitable. Although steel tanks can be heated from outside, they are usually heated by means of coils. Steam jets for heating the solution have the advantage of contributing considerably to the agitation. The jets are usually in the bottom of the tanks, permitting the steam to rise through the bath, thus heating it very efficiently. One objection to this type of heating is the water condensed from the steam which may dilute the solution. A certain amount, however, is not objectionable, since it makes up for the water evaporated from the bath. A balance is difficult to maintain, however, and the use of the steam jet is not popular.

In plants where waste steam is not available, combustion gases are sometimes used to heat the bath. Pipe coils enter the bottom of the tank and rise as a stack above it. Gas is burned at the lower end of the coil, the products of combustion and heat passing up through it, thereby heating the bath. This type of installation has become quite popular in certain localities.

The cleaner solution varies with the cleaning problem and, therefore, cannot be definitely specified. Having selected a cleaner and the strength to be used (possibly eight ounces per gallon), the usual procedure of making up a bath is to fill the tank about one-half full of water and heat to boiling. The cleaner is then added slowly (too rapid addition may cause spattering from the formation of steam) and scattered over the surface. Water is finally added to bring the solution up to the working level and the bath is then heated to boiling. If the bath does not boil, some other form of agitation is necessary. The bath is sometimes agitated by forcing air in at the bottom of the tank. In other shops mechanical plungers are employed, but if a boiling solution is used and the tank is properly designed, additional agitation is not necessary.

The amount of cleaner to be added to the bath during use depends upon the amount and condition of the ware. This can be determined to a certain extent by titrating with acid or using cleaner pills as described on page 103. A cleaner bath, however, becomes loaded with grease and oils which make it unsatisfactory for use. The water break test described on page 103 is the most satisfactory, because it is a simulated service test. Fresh cleaning solutions should be made whenever necessary, as good work cannot be done with poor solutions.

Rinsing. Rinsing is an essential part of the cleaning. The ware comes from the cleaner bath with a thin layer of cleaner on its surface and in the pores of the metal. This layer must be rinsed off thoroughly, since it would produce oil on the ware if carried over into the acid pickle solution. The rinse is preferably made in running water, the warmer the better. A still bath, even if hot, does not make a good rinse. The ware on entering the rinse loses its film of cleaner which tends to rise to the surface of the bath and, if the circulation is good, this layer should float off the bath to the overflow before the ware is withdrawn from the rinse. If the ware is dipped in the rinse and removed without allowing the surface to clear, it is liable to take up some of the cleaner again on removal from the bath. A good rinse not only puts the ware in a better condition for pickling, but it eliminates the danger of contaminating the pickle bath with cleaner solution.

Pickling. Pickling tanks differ from cleaner tanks in that they must withstand hot acid solutions. Wood, lead-lined, or acid-proof stoneware tanks are used. The wooden tanks are usually of cypress, built quite heavy with acid-proof tie rods. Lead-lined wooden tanks are used to some extent although they are not as common as the former. The lead lining must be protected by wooden guard strips to avoid being damaged by the pickle baskets. The same precautions as mentioned for the cleaner tanks should be considered in the design or selection of the acid pickle tanks. Acid-proof stoneware, tile, or brick tanks are sometimes used for large installations, but the multiplicity of the joints is objectionable. Sulphur cements or acid-proof hydraulic cements are used to bond the bricks, the joints being made as close and tight as possible. The whole tank is usually built inside of concrete retaining walls, with lead, tar, or cement backings. Alloy metal tanks, although suitable for small installations, have not been used for large scale production because of their cost.

Pickle solutions are heated by means of lead steam coils or live steam jets. The lead coils are installed either in the bottom or along the side of the tank and are protected by wooden strips. A special grade of lead is used for this purpose as the ordinary lead pipe is pitted by the acid. The open steam jet serves very well and is quite common in enamel shops. It agitates the bath but it has a tendency to dilute the acid solution.

When using sulphuric acid for pickling, the bath is heated to 140-150° F and is held at about that temperature. The rate of pickling

drops if the temperature is lowered and the fumes become excessive if temperatures exceed this range.

To make a bath, the water is first added in the tank and then the acid is poured in. The reverse procedure is dangerous, for the addition of water to sulphuric acid heats suddenly, forming steam, causing an explosion. A solution containing about six per cent by weight of sulphuric acid is used in enamel shops. Table 13 gives

TABLE 13
AMOUNTS OF WATER AND COMMERCIAL ACID REQUIRED FOR PREPARING
ONE HUNDRED GALLONS OF PICKLE SOLUTION *

Per cent Acid (by weight)	SULPHURIC ACID		MURIATIC ACID	
	Gallons 66° Baumé sp. gr. 1.835	Gallons 60° Baumé sp. gr. 1.706	Gallons 20° Baumé sp. gr. 1.160	Gallons 18° Baumé sp. gr. 1.142
1%	0.58	0.76	2.75	3.10
2%	1.18	1.53	5.50	6.20
3%	1.79	2.32	8.33	9.40
4%	2.40	3.10	11.15	12.58
5%	3.01	3.90	14.00	15.78
6%	3.66	4.70	16.90	19.05
7%	4.30	5.53	19.80	22.32
8%	4.95	6.38	22.75	25.65
9%	5.60	7.20	25.70	29.00
10%	6.23	8.06	28.70	32.40
11%	6.91	8.94	31.75	35.80
12%	7.60	9.82	34.80	39.25
13%	8.29	10.70	37.85	42.70
14%	8.98	11.60	40.95	46.20
15%	9.66	12.50	44.10	49.70
One gallon contains				
Lbs. of Commercial Acid	15.30	14.23	9.67	9.52
Lbs. of Pure Acid	14.29	11.06	3.05	2.66
Per cent Pure Acid	93.4	77.7	31.5	27.9

* Modified from page 299, J. E. Hansen. *Advanced Technique of Porcelain Enameling*, Enamelist Publishing Co. (1932).

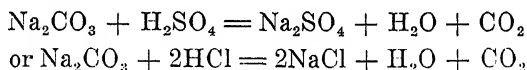
the amounts of commercial acids to be added in preparing one hundred gallons of pickle solution.

The amount of acid to be added from time to time during use is determined by the amount of ware which is pickled. The acid strength is determined by titration with standard alkali and the ferrous sulphate content by titration with potassium permanganate. The pickle-pill method is also satisfactory. These methods are described on page 104.

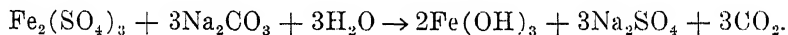
Hydrochloric acid (muriatic acid) is generally used as a cold solution, the vapors being very pungent if it is heated. It is generally used as a solution of about eleven per cent strength which pickles fairly fast, but not as fast as the hot sulphuric acid bath. At 90° F it pickles very rapidly and efficiently, but if heated to higher temperatures it corrodes the lead pipes. The solution is usually made by adding the acid to the water, thus not exposing the tank to the concentrated acid.

Rinsing. The rinse following the pickle solution should be a bath of running water, preferably hot, but usually cold. This removes the acid from the pickled ware, the basket of ware usually being moved up and down to aid the process. The rinse should be always in running water to avoid building up an acid content. Acid remaining on the ware, even in minute quantities, causes excessive rusting and enamel blisters. If the ware is not thoroughly rinsed, acid will be carried over into the neutralizing tank and will weaken this bath very rapidly, with a formation of salts which are objectionable.

Neutralizing. The neutralizing bath is designed to remove the last traces of acid in the pores of the metal. It is a solution of 0.3 to 0.4 per cent alkali (Na_2O), being composed of soda ash, borax, or trisodium phosphate and water. The bath should always be used hot (150-160° F), for the heat contributes to the rapid interaction of the acid and the alkali. The reaction which takes place in the neutralizing is about as follows:



The neutralizing solution, therefore, builds up a concentration of sodium sulphate or sodium chloride. In addition, if any appreciable ferrous sulphate is carried over it may be oxidized to ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, which reacts with the soda ash, Na_2CO_3 as follows:



This reaction adds more sodium sulphate to the solution and precipitates ferric hydroxide. Some of this ferric hydroxide undoubtedly remains on the ware as a straw colored rust.

If the water from which the neutralizing solution is made is hard, it contains calcium and magnesium salts which react with the alkali to form insoluble carbonates. These carbonates with the ferric hydroxide will float as a scum on the solution and should be skimmed

off. If the water is hard, it is good practice not to heat the neutralizing solution to boiling, since at lower temperatures these carbonates tend to settle to the bottom of the tank and remain there.

Too low a concentration of neutralizer should be avoided as it will not rapidly neutralize all of the acid, and too high a concentration is objectionable because the salts will be carried over with the iron and will "set up" the enamel slip.

Sometimes two neutralizing baths are used, the first being slightly stronger and the second slightly weaker than average. This, however, is not common and not often necessary.

Drying. The ware on removal from the neutralizing bath should be transferred immediately to the dryer. The dryer is preferably of the continuous conveyer type so that the ware need not be dried in batches. It should be dried rapidly and should, during this operation, be free from dust and other forms of contamination.

SPECIAL PROCESSES

In addition to the regular procedures for preparing the metal surfaces for enameling, other special operations are sometimes employed. In recent years the use of the nickel dip, introduced primarily for the preparation of sheets for white ground coats, has become more popular even when blue and black ground coats are used. It improves the adherence of white ground coats and tends to eliminate fishscale and copper heads in the cobalt ground coats.

The nickel dip follows the acid rinse after pickling and is itself followed by a rinse and the neutralizer ordinarily used as the last step in the preparation of the surface. The nickel dip bath is a solution of double salts, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and sufficient acid or base to give the desired hydrogen ion concentration. Several compositions which can be used are shown in Table 14.

These solutions are operated at temperatures of 160 to 195° F and the ware is left in the bath for five or ten minutes.

The control of the nickel bath is very important as the conditions must be just right to give satisfactory results. The deposit desired is a uniform dusty black coating which is very thin and has no projections. Any projections tend to cause dark spots in white ground coats and may be a source of blistering on additional coats if they extend through the ground.

The solution loses nickel on continued use and becomes loaded with iron. The nickel can be replaced from time to time but the iron is removed with difficulty. In ordinary practice daily addi-

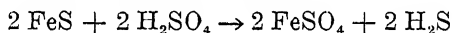
tions are made to rejuvenate the solution, but in time it becomes exhausted and further additions do not help it. ~~As the bath becomes old the iron in solution separates out as the hydroxide forming a brown sludge in the bottom of the tank. As the sludge accumulates it tends to form a scum on the ware which is difficult to wash off. In ordinary practice the bath is discarded at this point and a new one made up. However, Hansen ⁵ suggests the addition of ammonia to~~ ^{*SANGALOR}

TABLE 14
NICKEL DIP SOLUTIONS

	Ounces per Gallon of Water			
	I	II	III	IV
Double nickel salts.....	3.2	4.0	8.0	1.9
Boric acid.....	.52	.25	.25	.18
Ammonium carbonate.....	.35	.2521

the solution until a pH of 6.4 is reached and then heating at 180° F with air agitation. This oxidizes the iron to the ferric state and the alkaline solution converts it to the insoluble ferric hydroxide. The bath is then allowed to cool and the precipitate to settle. The nickel solution is siphoned off the sludge and the latter washed out of the tank and made up to proper strength. The control of the nickel dip solution is described fully on page 107.

The use of iron sulphide to aid the adherence, especially of gray ware enamels, is not very common. Iron sulphide added to the pickle solution reacts to form hydrogen sulphide gas.



This gas, which is acid in character, tends to etch the iron and gives a better surface for enamel adherence with a decrease in the tendency to fishscaling. The finely crushed iron sulphide is usually added to the bath each time a basket of ware is introduced into the solution.

The hydrogen sulphide gas which is evolved from the bath is obnoxious and poisonous and should not be breathed in any appreciable quantities, or it will cause severe vomiting and temporary sickness. Iron sulphide should not be used in the pickle solution unless excellent ventilation is provided. Any sulphur gases should be kept out of the enamel shop because of their effect on enamels. Hydrogen sulphide tends to convert lead in enamels to the black lead sulphide and the oxides of sulphur tend to form a scum on the ware during firing.

⁵ The Advanced Technique of Porcelain Enameling, Enamelist Publishing Company, Cleveland, Ohio.

CONTROL

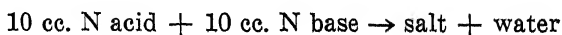
The control of the cleaning and pickling operations is essential to good work and economical operation. The use of solutions which are too strong or too weak, too hot or too cold, or the discarding of solutions without knowing their conditions results only in low efficiency. The ware is not properly processed and the best has not been obtained from these baths. Scientific control is becoming more common and is a part of all modern operations. The amount of equipment necessary and the time required for such control is not great; therefore the cost of control is small.

Theory. The testing of cleaner, pickle, and neutralizer solutions is based on the acidity or alkalinity of the solutions, and on the quantities of by-products present in the solutions. The pickle solution is acid and the cleaner and neutralizer solutions are basic. To test the acidity or alkalinity of the solutions a standard (known strength) solution is compared with the unknown by titration. Certain dyes, called indicators, such as methyl orange, phenolphthalein, and litmus, show different colors in basic and in acid solutions, thus:

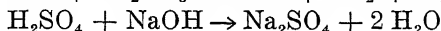
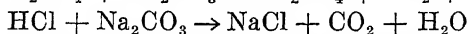
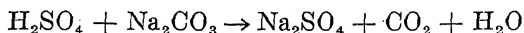
	<i>Basic</i>	<i>Acid</i>
Methyl orange.....	Yellow	Red
Phenolphthalein.....	Red	Colorless
Litmus.....	Blue	Red

At the point where the color change occurs, neutral conditions exist (the solution is neither acid nor basic but neutral). The test of an acid solution, therefore, involves the addition of known amounts of a standard basic solution in the presence of an indicator until there is a color change. Knowing the strength of the basic solution added, the strength of the acid can be calculated. Normal solutions are standard solutions containing one equivalent weight of the substance in a liter of solution.

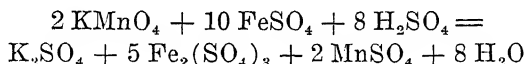
For example, a normal solution of sulphuric acid contains 49 grams of H_2SO_4 dissolved to one liter in water. The equivalent weight of sulphuric acid is one-half of the molecular weight ($98 \div 2 = 49$). A tenth normal solution, N/10, of sulphuric acid contains one-tenth of the equivalent weight, a half normal, N/2, one-half of the equivalent weight of sulphuric acid dissolved to one liter in water. Normal solutions are equivalent to one another. For example, ten cubic centimeters of normal acid will neutralize ten cubic centimeters of normal base.



The salt and the water give a neutral reaction toward the indicators. Examples of actual chemical reactions in testing cleaner and pickle solutions are as follows:



The testing of the iron content of the acid solution is based on the oxidation of ferrous sulphate (FeSO_4) to ferric sulphate ($\text{Fe}_2[\text{SO}_4]_3$). Potassium permanganate (KMnO_4) solution is used for this purpose. The reaction is indicated by the following equation:



Thus, two molecules of KMnO_4 are equivalent to ten molecules of FeSO_4 in the reaction. If the amount of KMnO_4 used to oxidize the FeSO_4 of an unknown solution is known, the amount of FeSO_4 present can be calculated. In the titration of the unknown pickle solution with potassium permanganate, the red color of the potassium permanganate solution is destroyed when it reacts with the ferrous sulphate. The first excess over the amount required to oxidize all of the ferrous sulphate to ferric sulphate contributes a pink color to the unknown, which establishes the end point.

The preceding discussion of acidity, alkalinity, and oxidation chemistry is not complete, but it should give some understanding of the basic principles involved in pickle and cleaner bath control. To control these baths in practice, however, no knowledge of the theory is necessary. If solutions are made according to direction and the titration is carried out carefully, the whole process is quite simple.

The requirements of good control methods are simplicity, the necessary accuracy, rapidity, and low cost. The following methods, although not extremely precise, are much more accurate than is necessary and are simple to the extent that almost any one of reasonable intelligence can use them.

Cleaner Control. The chemical cleaning solution should be controlled for its alkali content and for the amount of oil and grease accumulated in the bath.

The determination of the alkali content requires only a simple titration. Suppose the cleaner solution contains six ounces of cleaner to the gallon. This then should be titrated with acid solution in the presence of methyl orange indicator. With a pipette place ten cubic

centimeters of the fresh cleaner solution in an Erlenmeyer flask. Dilute to about forty cubic centimeters and add three drops of methyl orange indicator, which will turn the solution yellow. Next fill a glass-stoppered burette with a standard solution of sulphuric acid. This acid solution should be of such a strength N or $N/2$,[†] that it can be duplicated whenever necessary. Acids of known strength can be obtained at almost any supply house. The burette containing the acid solution should be filled just to the zero mark.

The next step is to titrate the acid slowly into the unknown solution, shaking gently, but not allowing it to spatter. Where the acid falls into the solution the color will change, but additions are made just to the point where there is a permanent change from yellow to orange or red on gently shaking. The first permanent appearance of the orange-red color indicates that the end point is slightly past. On obtaining the end point read the burette to determine the amount of acid used. Suppose this reads twelve cubic centimeters. Then twelve cubic centimeters of acid of the strength used are equivalent to ten cubic centimeters of the cleaner solution. Since we know in this particular case, where a new cleaner solution is used, that it contains six ounces to the gallon, then ten cubic centimeters of a six-ounce per gallon cleaner solution requires twelve cubic centimeters of acid solution for neutralization. Dividing six into twelve, we find that each ounce of cleaner added to the cleaner solution requires two cubic centimeters of acid solution. We have thus standardized our acid on the basis of the cleaner solution as made up. The next step is that of dividing the twelve cubic centimeter volume on the burette into six divisions, marking them from the bottom up, 0, 1, 2, 3, 4, 5, and 6 ounces. The equipment is now prepared for the control of the cleaner solution.

If ten cubic centimeters of an old cleaner solution are now titrated with the standard acid in the same manner as for the new one, the amount of acid required to reach the end point will be less than twelve cubic centimeters, or point zero. Suppose, for example, only eight cubic centimeters, or point two, will be reached when the end point is obtained. This indicates that the cleaner solution is deficient in alkali to the extent of two ounces of cleaner per gallon. The proper amount, two ounces per gallon, of cleaner is then added to bring the strength up to six ounces per gallon. The conversion of ounces per gallon present in the cleaner to pounds to be added to the tank can

[†] A normal (N) solution can be made half normal ($N/2$) by diluting with an equal volume of distilled water. Any normality less than N can, therefore, be obtained by pr dilution.

be conveniently calculated in advance and put in the form of a chart near the cleaner tank.

The equipment for testing the cleaner solution, therefore, consists of a shelf space one by two feet, a glass-stoppered burette (preferably of the refillable overflow type), an Erlenmeyer flask (250 cc.) a ten cubic centimeter pipette, a bottle of methyl orange indicator, a supply of standard acid, and a supply of distilled water.

An outline of the test directions follows:

1. Pipette ten cubic centimeters of cleaner solution into a clean Erlenmeyer flask.
2. Add forty cubic centimeters of distilled water.
3. Add three drops of methyl orange indicator.
4. Fill burette to the zero mark with standard acid.
5. Titrate to the end point (change in color from yellow to orange).
6. Read off strength of cleaner from the burette.
7. From the chart determine the amount of cleaner to be added to the tank.
8. If an open-end burette is used return the standard acid to the supply bottle, or preferably stopper the burette.

Another simple method for determining the alkalinity is that of using cleaner pills. In this method a ten cubic centimeter aliquot of the cleaner solution is diluted with about forty cubic centimeters of distilled water. To this the cleaner pills are added, counting the number used until the solution changes color. These pills contain acid (usually boric acid) and an indicator. Each pill, which is often a capsule containing powder to be emptied into the solution, is equivalent to a certain strength when added to ten cubic centimeters of the solution. For example, if one pill is required for each ounce of cleaner per gallon, then a six-ounce per gallon solution should require six pills. If it requires only five the solution is weak and should have an additional ounce per gallon of cleaner added to it. These test pills are convenient and sufficiently accurate for control, but they are more expensive than the titration method.

Since the cleaner bath may be sufficiently alkaline, but may at the same time contain an excessive amount of oil and grease, it should be tested for the latter. There is no method entirely satisfactory for this purpose, but that of determining the water-breaks is useful. The method of doing this is to use a sheet of metal one foot square, dip it in oil, drain and determine the length of time required

to clean it in the solution. Usually a mineral oil or one difficult to remove is used and the tests are made daily, the time required lengthening as the cleaner becomes old. By coördinating these times with practice a comparison can be set up for the particular conditions to determine when the solution is exhausted. Such tests are indications which, as one grows more familiar with them, become very useful.

Control of the Neutralizer Solution. The neutralizer solution can be controlled in a manner similar to that used for the alkali cleaner. It is, however, much more dilute and to obtain accuracy a larger sample (100 cc.) is necessary. If exactly normal acid is used as the standard solution, each cubic centimeter will equal .031 gram of Na_2O , and if a 100 cubic centimeter sample of neutralizer is used in the titration, each cubic centimeter of acid will equal .031 per cent of Na_2O in the neutralizer bath.

Neutralizer pills can be obtained and can also be used in a similar manner to cleaner pills.

Pickle Acid Control. The control of the pickle solution involves determinations of its acidity and the ferrous sulphate content. This can be done by either the titration or the pickle pill method. †

In the titration of acidity, standard normal sodium hydroxide is used and methyl orange serves as the indicator. The simplest method of standardizing the equipment is as follows: Take a ten cubic centimeter sample of the fresh pickle solution of known strength and place it in a 250-cubic centimeter Erlenmeyer flask with forty cubic centimeters of distilled water and three drops of methyl orange indicator.

Fill a rubber tipped burette with the standard normal sodium hydroxide solution and titrate to the change in color from red to yellow. The flask should be shaken gently and the first permanent yellow color indicates the end point. Read the burette. If twelve cubic centimeters of alkali have been used to neutralize ten cubic centimeters of the acid solution, which will be assumed for explanation to be a six per cent acid bath, then the twelve cubic centimeters equal a strength of six per cent acid. The burette should then be divided into six divisions over the twelve cubic centimeter space, marking the divisions from zero to six from the lowest one up. In titrating unknown solutions the reading on the burette will indicate the per cent of acid necessary to bring the acid in the tank up to strength. A chart should be calculated showing the number of gallons of the acid required to bring the solution up to strength when 1, 2, 3, 4, 5, or 6 per cent is needed.

An outline of the test directions is as follows:

1. Pipette ten cubic centimeters of the acid solution into a clean Erlenmeyer flask.
2. Add forty cubic centimeters of distilled water.
3. Add three drops of methyl orange indicator.
4. Fill burette to the zero mark with standard alkali.
5. Titrate to end point (change from red to yellow color).
6. Read off the amount of acid to be added as indicated by the burette.
7. From the chart determine the number of gallons of acid to be added to the tank.
8. Empty and rinse the burette.

The equipment necessary for the control of the acidity of the pickle bath is, therefore:

- One rubber tipped burette
- One Erlenmeyer flask (250 cubic centimeters)
- One pipette (ten cubic centimeters)
- One bottle of methyl orange
- One supply bottle of N sodium hydroxide
- One supply bottle of distilled water.

Pickle pills * can be used for the control of the acidity of the pickle bath. They are usually filled with sodium carbonate and methyl orange and act faster in a hot solution. To make the test a ten-cubic centimeter aliquot of the pickle solution is transferred to a flask and forty cubic centimeters of warm water are added. The pills are then slowly placed in the solution, keeping count. The end point is the change from the red to the yellow color. If a six per cent acid requires six pills to neutralize ten cubic centimeters, then each pill represents one per cent of acid. The ratio between acid strength and the number of pills must be first established and then the amount of acid required can be readily calculated. Pickle pills are very satisfactory and often used.

Determination of the Ferrous Sulphate Content of Pickle Solutions. The determination of the amount of ferrous sulphate or ferrous chloride in a pickle solution is based on the determination of the amount of an oxidizing reagent necessary to convert the iron salts from the ferrous to the ferric state. Potassium permanganate is a suitable reagent for this purpose.

* Pickle pills are capsules containing a measured amount of reagent. The use of these pills permits the addition of the reagent in measured amounts without the use of a chemical balance. Knowing the strength of each capsule the number of capsules gives the total strength of the reagent added.

A normal solution (31.6 grams per liter) is generally employed for this purpose. It is usually standardized with Mohr's salt (ferrous ammonium sulphate) in the following manner: A five-gram sample of ferrous ammonium sulphate is accurately weighed and dissolved in a solution of sulphuric acid (forty cubic centimeters of water, five cubic centimeters of sulphuric acid) and is then titrated with the potassium permanganate solution with constant stirring until the first excess of the permanganate is shown by the appearance of a permanent pink color in the solution being titrated.

Mohr's salt has the formula $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and contains 13.95 per cent of iron. A five-gram sample of Mohr's salt, therefore, contains $5 \times 13.95/100 = 0.698$ gram of iron. If fifteen cubic centimeters of the permanganate solution are required to oxidize all of the ferrous iron in the Mohr's salt, then each cubic centimeter of permanganate is equivalent to $0.698/15 = .0465$ gram of iron. If ten cubic centimeter samples of pickle solution are titrated, then the number of cubic centimeters of permanganate solution required, multiplied by the amount of iron each cubic centimeter is equivalent to (.0465), indicates the total iron in the sample.

To determine the iron content of the pickle bath, place ten cubic centimeters of the solution in a beaker and add five cubic centimeters of sulphuric acid dissolved in forty cubic centimeters of water. Fill a burette with standard permanganate solution and titrate, with constant stirring, until the first pink color appears. Read the burette and calculate the iron content of the pickle bath. In most practice the iron is not permitted to exceed six per cent and is seldom allowed to exceed eight per cent.

An outline of the test directions is as follows:

1. Pipette ten cubic centimeters of the pickle bath into a 300 cubic centimeter beaker.
2. Add five cubic centimeters of sulphuric acid dissolved in forty cubic centimeters of water.
3. Fill the burette to the zero mark with the standard potassium permanganate solution.
4. Titrate, with constant stirring, to the first permanent pink color.
5. Read the burette and determine the iron content.

It is often convenient to construct a chart for converting burette reading to per cent iron in the tank.

The equipment necessary for the control of the iron content of the pickle bath is as follows:

One glass-stoppered burette
 One 300 cubic centimeter beaker
 One glass stirring rod
 One pipette (ten cubic centimeters)
 One supply of standard potassium permanganate (can be obtained at supply houses).

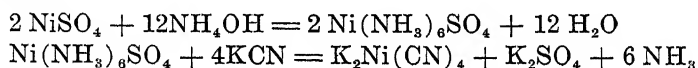
The pill method can also be used for determining the iron content of the bath. These capsules contain potassium permanganate crystals. To a ten cubic centimeter sample of the bath add five cubic centimeters of sulphuric acid in forty cubic centimeters of water. Add the pills (called iron pills) one by one while stirring the solution until the first permanent pink color appears. The number of pills indicates the iron content.

Control of the Nickel Solutions. The nickel solutions should be controlled both for the nickel content and for the hydrogen ion concentration.

The titration of acidity and alkalinity does not give the hydrogen ion concentration when complete ionization does not exist. In the operation of a nickel solution the hydrogen ion concentration is of primary importance. It should have a pH value between 5.6 and 6.4, seven being neutral, below seven acid, and above seven basic.* The boric acid gives the proper acid content to the original solution, but on use a certain amount of pickle acid is carried over into the nickel bath. Thus, if the pH falls below 5.6, the solution must be neutralized by the addition of ammonia. Although the solution does not usually become too alkaline, small amounts of boric acid can be added to bring the pH below 6.8.

The pH value of the solution is generally determined by the colorimetric method although the electrometric method is more accurate. The colorimetric method, however, is simple and requires much less equipment, which can be obtained on the market in different types. Brom-phenol Red and Brom-cresol Purple cover the range from 5.2 to 6.8, and Alizarin covers the range 5.5 to 6.8, so that the use of either dye is satisfactory.

The nickel content of the solution is determined by titrating with a standard potassium cyanide solution in the presence of silver nitrate, ammonium sulphate, ammonia, and potassium iodide. The reactions are as follows:



* The pH value is the negative log of the hydrogen ion concentration.

The silver nitrate and potassium iodide react in the solution, forming a flocculent white precipitate of silver iodide. This is used for determining the end point of the reaction between the nickel sulphate, ammonia, and potassium cyanide. As soon as the cyanide is in excess the silver iodide precipitate dissolves. Sodium pyrophosphate is added to keep any iron present in solution. Sometimes citric or tartaric acid is used for this same purpose.

The solutions required for the determination are as follows:

1. Potassium iodide, about 0.5 N. (83 grams of potassium iodide per liter).
2. Potassium cyanide solution, about 0.5 N. (32.6 grams of potassium cyanide and 1.7 grams of silver nitrate per liter). Label "Poison."
3. Sodium pyrophosphate, about 2 N. (133 grams of sodium pyrophosphate per liter).

Method: To ten cubic centimeters of the nickel solution five grams of ammonium chloride and fifty cubic centimeters of the sodium pyrophosphate solution are added. The solution is then made alkaline with ammonium hydroxide and one cubic centimeter of the potassium iodide solution is added, whereupon it is titrated at room temperature until the white precipitate just disappears. The cyanide solution must be standardized on a solution containing a known amount of nickel.

Example: Suppose a given nickel solution contains .2064 gram of nickel in fifty cubic centimeters and on titrating it 32 cubic centimeters of the cyanide solution is required to reach the end point. Then one cubic centimeter of the solution is equivalent to $.2064/32 = .00645$ gram of nickel.

If ten cubic centimeters of the nickel flash solution requires 36.5 cubic centimeters of the cyanide solution its nickel content must be $36.5 \times .00645 \times 1000/10 = 23.5$ grams of nickel per liter. To change grams of nickel to grams of double salt multiply by 6.73.

SAND BLASTING SHEET STEEL

Sheet iron and steel are sandblasted only when large shapes or heavy stock are used. It gives a satisfactory surface for enameling, but warps and distorts thin stock. For iron or steel, which are not as hard and brittle as cast iron, the pressure of the sand blast must be low to prevent embedding the particles in the metal. Sand is in general more suitable than steel grit for sheet metal, for the latter embeds itself and causes copper heads. A full discussion of blasting is given under the preparation of cast iron surfaces for enameling.

PREPARATION OF THE SURFACE OF CAST IRON FOR ENAMELING

The preparation of cast iron surfaces for enameling is quite different from sheet metal practice because they do not pickle well and are most satisfactorily cleaned and prepared for an enamel coating by blasting. The rough edges, gates, and molding sand are first removed and then the surface is thoroughly sand blasted.

Cast iron, even with the best foundry practice, comes to the enameler with irregularities of surface and a hard skin which must be roughened or removed. This thin skin-like surface is harder than the body of the casting and it does not enamel well. If entirely removed, there is a decided decrease in the tendency for the enamels to blister during firing. A well cleaned casting is essential to good cast iron enamels.

Blasting (Sand Blasting). Blasting is an operation in which abrasive grains are thrown forcibly against the ware by means of a blast of air or other gas. Air is used almost exclusively for the cleaning of castings, but the abrasives vary. Three types of abrasives are used: sand, steel grit, and steel shot. The first two, sand and steel grit, are used for blasting castings to be enameled. In common practice the air under pressure and laden with sand or steel grit escapes through a nozzle, throwing the abrasives with great force. These thousands of small particles striking the casting, remove the scale and roughen the surface to a velvety finish. Such a finish is readily enameled, since it is clean and the enamel adheres well to it.

The most important consideration to the enameler is that the blasting be thorough and efficient. If it is not thorough many enamel defects will result and it cannot be efficient.

The cost of blasting is considerable and can be divided as follows:⁶ overhead and labor 65 per cent, power for air 20 per cent, and abrasive cost 15 per cent. These proportions will vary under different conditions, the selection of equipment and the operation being of great importance.

Blasting involves numerous intricate problems of air flow, ventilation, air floating of abrasives, dust separation, and the effects of design.

The nozzle furnishes the orifice which controls the air and permits the air to give the abrasive its high velocity. Its design and life, therefore, is of great importance. Nozzles for different purposes vary greatly in size and shape. The diagrams in Figure 44 show the ex-

⁶ Edward H. Stehman, *Enamelist* 5, (5) 26 (1928).

tremes in shape. The most common shape of nozzle is shown as b, with a bore about one-sixth its length. It is uniform in diameter when new, but the wear tends to taper it from the outlet end to the inlet as shown by the cross section. This tapering continues until an angle of three degrees is reached and then the entire surface wears away. It is evident that the inlet end of the nozzle acts as the orifice for the air and does not change until after the three-degree taper is established. As this orifice enlarges, however, the efficiency of the nozzle is reduced as indicated by Table 15. If the orifice is, for example, enlarged from $\frac{1}{4}$ to $\frac{5}{16}$ inches in diameter, at sixty pounds pressure, the air flow increases from 67 to 105 cubic feet per minute, which, with power at three cents per KWH, increases the cost from 33.2 to 52.1 cents per hour. This represents an increase of nearly 57 per cent in the power cost. It is thus evident that the wear of the nozzle increases operating costs much greater than nozzle replacement cost. In addition the blasting done after the nozzle is worn is not as good as it was with the newer nozzle. Since the ordinary chilled cast iron nozzles do not last longer than an hour, other types have come on the market made of carboloy, and boron nitride. These nozzles, although expensive, last hundreds of hours and are much more suitable for automatic machines. Some users also find them more economical.

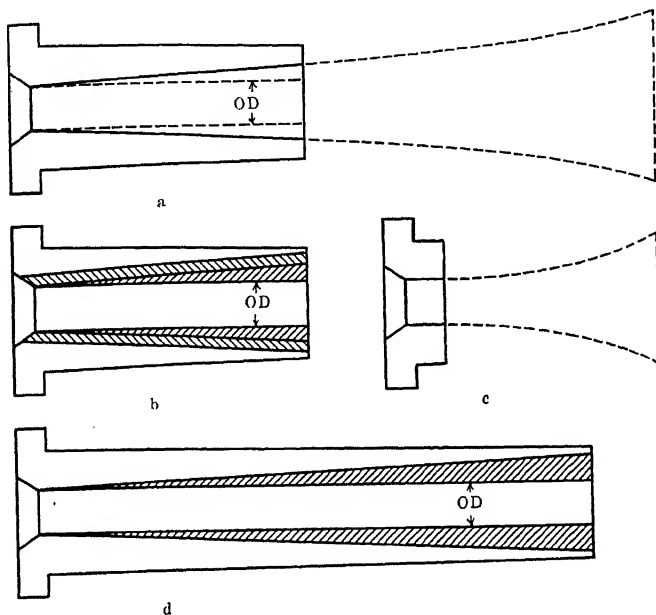
The spread of the abrasive from the common type of designed nozzle is shown by the dotted lines of a in Figure 44. If the length of a nozzle is increased, the amount of metal which must be worn away to form the three-degree angle is much greater and the life of the nozzle is increased proportionally, but with the greater length the frictional resistance of the nozzle is increased, reducing its efficiency. Such a nozzle is shown in d of Figure 44.

If the other extreme is approached and the nozzle is made very short, as shown by c of Figure 44, the wear is again reduced. In this case, however, the abrasive is not concentrated at so small a point as it leaves the nozzle but it spreads and loses its force. Where the ware to be blasted does not require a very severe blast, as in the sheet iron industry, such a nozzle is sometimes satisfactory.

The distance of the nozzle from the ware is an important consideration. The abrasive as it leaves the nozzle is given an acceleration by the air until it reaches a maximum for the conditions. This point, where the maximum is attained, is the distance from the nozzle where the most efficient work is done. In general practice it is from twelve to fifteen inches, but it varies with conditions. The point of

maximum efficiency is often taken as that distance at which a blue haze appears where the grains strike the casting.

In Table 15 the air flow is shown for different pressures and orifice openings when no abrasive is flowing. When sand is used approximately thirty per cent less air is discharged and when steel



OD=Original Dimensions

FIGURE 44. The Wear of Nozzles.

grit is used approximately sixteen per cent less air is used. With smaller nozzles the reduction of air, when abrasive is present, is usually less and with larger nozzles it is usually greater.

Edward H. Stehman ⁷ reports a series of tests on nozzle sizes, air consumption pressures and blasting times with enamel castings and shows the importance of such studies in controlling costs.

Figure 45 gives the air consumption, the power, and the time required for cleaning stove castings at different pressures. This shows that an increase in pressure is not always accompanied by an increase of efficiency.

Another example of such a study is shown in Figure 46 where bowls were sandblasted with $\frac{1}{4}$ - and $\frac{3}{8}$ -inch nozzles at different pressures. The $\frac{3}{8}$ -inch nozzle at fifty pounds consumed about the same

⁷ *Ibid.*

volume of air as the $\frac{1}{4}$ -inch nozzle at 75 pounds, but it effects a reduction of 47.5 per cent in the blasting time and 53.5 per cent in the air power. Thus the $\frac{3}{8}$ -inch nozzle in this case shows not only increased production but also decreased sand blasting cost. Stehman figures the actual savings as follows:

Saving in sandblasting time 3.41 hours per ton of metal cleaned, at \$1.00 per hour plus 100 per cent overhead.....	\$ 6.82
Saving in air power cost 91.5 H. P. hrs. per ton of metal cleaned, at 2 cents per H. P. hr.	1.83
Total saving per ton.....	\$ 8.65

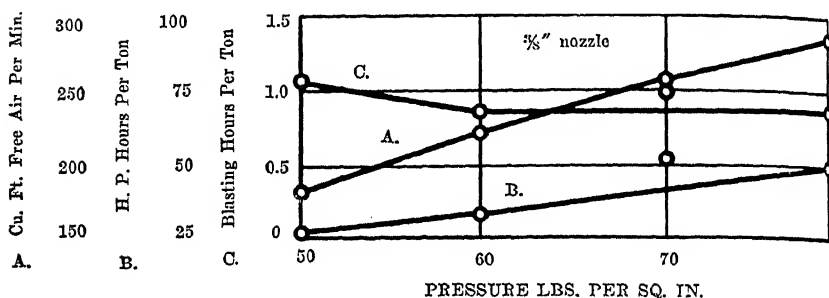


FIGURE 45. Air Consumption, Air-power and Blasting Time at Different Pressures.*

These data show the importance of efficient sand blast operation and equipment. The conditions of blasting other than pressure, nozzles, and equipment make the establishment of general rules very difficult. However, it must be remembered that the hardness of the surface of the casting, the amount of surface to be removed, the shapes of the castings, and the characteristics of the operator influence blasting efficiency. Each blasting problem should be treated separately, and, when the most satisfactory conditions are acquired, they should be strictly adhered to.

• The character of the surface of the casting influences the pressure required. A hard surface requires high pressure, and a softer surface, a lower one. Sheet iron for example is sand blasted only at relatively low pressures to avoid the danger of embedding abrasives in the metal. When high pressures or coarse abrasives are used the blasted surface is relatively rough. The design of the nozzle and the distance of the

* *Ibid.*

TABLE 15

SAND BLAST OPERATING COSTS IN CENTS WITH VARYING ORIFICES, PRESSURES, HORSE POWER, AND UNIT CHARGES FOR POWER.

Gauge Pressure	Nozzle	Air Cu. Ft. per Min.	1.5		2.0		2.5		3.0	Kw. per Cu. Ft. Free Air Per Min.	Horse Power (Estim.)
			Per Hr.	Per 1,000	Per Hr.	Per 1,000	Per Hr.	Per 1,000	Per Hr.		
30	$\frac{3}{16}$	22.4	2.82	2.10	3.75	2.80	4.70	3.50	5.63	4.20	2.3
	$\frac{1}{4}$	40.0	5.04	2.10	6.72	2.80	8.40	3.50	10.0	4.20	4.1
	$\frac{9}{16}$	62.5	7.90	2.10	10.5	2.80	13.2	3.50	15.8	4.20	6.4
	$\frac{3}{8}$	90.0	11.3	2.10	15.2	2.80	19.0	3.50	22.7	4.20	9.2
	$\frac{7}{16}$	123.0	15.4	2.10	20.6	2.80	25.7	3.50	31.0	4.20	12.6
40	$\frac{1}{2}$	161	20.4	2.10	27.2	2.80	34.0	3.50	40.8	4.20	16.6
	$\frac{3}{16}$	27.4	4.50	2.73	6.02	3.64	7.53	4.55	9.03	5.46	3.2
	$\frac{1}{4}$	49.1	8.00	2.73	10.7	3.64	13.4	4.55	16.0	5.46	5.9
	$\frac{9}{16}$	78	12.8	2.73	17.1	3.64	21.4	4.55	25.7	5.46	9.3
	$\frac{3}{8}$	110	18.2	2.73	24.3	3.64	30.3	4.55	36.4	5.46	13.4
50	$\frac{7}{16}$	150	24.7	2.73	33.0	3.64	41.2	4.55	49.4	5.46	18.3
	$\frac{1}{2}$	196	32.6	2.73	43.5	3.64	54.3	4.55	65.2	5.46	23.9
	$\frac{3}{16}$	32.8	6.24	3.16	8.32	4.22	10.4	5.27	12.5	6.33	4.5
	$\frac{1}{4}$	58.2	11.0	3.16	14.7	4.22	18.4	5.27	22.1	6.33	7.9
	$\frac{9}{16}$	91	17.3	3.16	23.0	4.22	28.8	5.27	34.6	6.33	12.4
60	$\frac{3}{8}$	130	24.7	3.16	33.0	4.22	41.2	5.27	49.4	6.33	17.8
	$\frac{7}{16}$	177	33.7	3.16	44.9	4.22	56.2	5.27	67.4	6.33	24.3
	$\frac{1}{2}$	232	44.1	3.16	58.8	4.22	73.5	5.27	88.2	6.33	31.7
	$\frac{3}{16}$	37.5	7.97	3.54	10.6	4.72	13.3	5.90	15.9	7.08	5.7
	$\frac{1}{4}$	67	14.2	3.54	19.0	4.72	23.7	5.90	28.5	7.08	10.2
70	$\frac{9}{16}$	105	22.3	3.54	29.8	4.72	37.2	5.90	44.7	7.08	16.1
	$\frac{3}{8}$	151	32.1	3.54	42.8	4.72	53.4	5.90	64.2	7.08	23.1
	$\frac{7}{16}$	205	43.6	3.54	58.2	4.72	73.7	5.90	87.3	7.08	31.5
	$\frac{1}{2}$	268	56.8	3.54	75.3	4.72	94.8	5.90	113.7	7.08	41.0
	$\frac{3}{16}$	42.9	10.0	3.90	13.3	5.20	16.7	6.50	20.0	7.80	7.2
80	$\frac{1}{4}$	76	17.7	3.90	23.6	5.20	29.6	6.50	35.4	7.80	12.7
	$\frac{9}{16}$	119	27.8	3.90	37.0	5.20	46.3	6.50	55.6	7.80	20.0
	$\frac{3}{8}$	171	39.9	3.90	53.2	5.20	66.6	6.50	79.8	7.80	28.7
	$\frac{7}{16}$	233	54.4	3.90	72.7	5.20	90.8	6.50	109.0	7.80	39.1
	$\frac{1}{2}$	304	71.1	3.90	94.8	5.20	118.2	6.50	141.9	7.80	51.1
80	$\frac{3}{16}$	47.5	12.1	4.23	16.2	5.64	20.3	7.05	24.3	8.46	8.6
	$\frac{1}{4}$	85	21.6	4.23	28.8	5.64	36.0	7.05	43.2	8.46	15.4
	$\frac{9}{16}$	153	33.8	4.23	45.1	5.64	56.3	7.05	67.6	8.46	24.0
	$\frac{3}{8}$	191	48.5	4.23	64.7	5.64	80.8	7.05	97.0	8.46	34.7
	$\frac{7}{16}$	260	66.1	4.23	88.2	5.64	110.0	7.05	132.1	8.46	47.3
80	$\frac{1}{2}$	340	86.3	4.23	115.0	5.64	144.0	7.05	173.0	8.46	61.8

nozzle from the work influences the pressure required, other conditions being constant.

The line resistance to the air flow and the leakage of the system increases the pressure required from the compressor. Since a very appreciable drop in pressure is often experienced between the compressor and the nozzle, the pressure gauge should be as close to the nozzles as is practicable.

• **Abrasives:** Since the introduction of steel grit there has been considerable controversy concerning the relative advantages of each

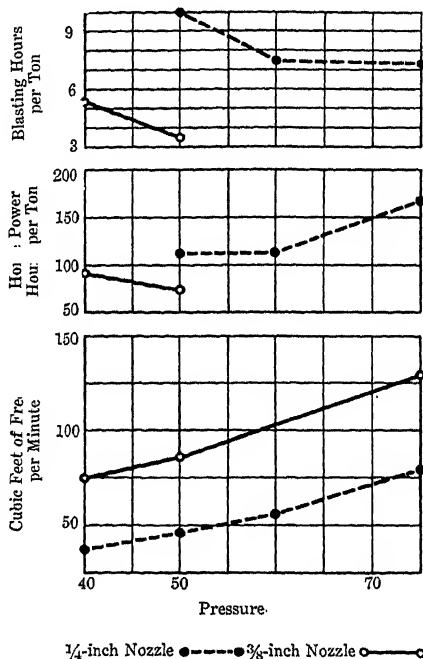


FIGURE 46.

Comparison of $\frac{1}{4}$ - and $\frac{3}{8}$ -Inch Nozzles at Different Pressures.†

for enameling work. Steel shot is not used for cleaning enameling irons because of its peening action which produces an unsuitable surface for enameling. ✓

Sand. The physical properties of the abrasive often limits the pressure to be used in sand blasting. Low grade sands must not be used at pressures of over sixty pounds or they will be shattered at the first impact. The higher grade sands will withstand higher pressures.

up to eighty pounds, and steel grit or shot will withstand as high pressures as are ever used in sand blasting. The efficiency of blasting depends upon the abrasive retaining its form as long as possible. If it shatters to a dust, its force is lost and the abrasive is destroyed so far as use for blasting is concerned. The dust is objectionable as it interferes with visibility and it must be removed from the abrasive. If not shattered the sand can be repeatedly used. The grains for sand blasting purposes are preferably round, the size varying with the work to be done. On soft iron the fine grains are most suitable while on hard iron the large grains are more efficient.

Steel Grit! Steel grit is a product manufactured by crushing and grading steel shot. A good grade has the structure of white cast iron and is very low in free carbon. It is angular, presenting many sharp corners and is very hard and strong. It resists shattering even at the highest pressures used for blasting and, therefore, produces a minimum of dust. Steel grit is two and one-half times as heavy as silica sand which gives it much greater inertia. It is more difficult to get it in motion but it exerts more force as it strikes the ware. The angular corners are considered desirable because of their cutting action, but as these wear down there is danger of peening the iron.

* Steel grit is produced in sizes from about 14 to 100 mesh, the finer being used for soft iron where a finely ground surface is desired and the coarse grains for hard service where a coarser finish is desired. In some operations the sizes of steel grit are blended to give the desired surface and in other operations silica sand is used with steel grit.

As automatic blasting equipment is becoming more common, thus making the labor cost a less important item, the consideration of the cost of the abrasive, the power, and the upkeep becomes more important.

* Steel grit and silica sand are used both alone and together for the cleaning of castings for enameling. For sheet iron or steel cleaning, the silica sand is in general preferable. Steel grit, if used at pressures sufficient to clean sheet iron rapidly, has a tendency to bury itself in the iron stock and cause copper heads in the enamel.

The selection of abrasives for cleaning metal surfaces for enameling should be based on the quality of the work done by the abrasive. A surface that can be depended upon to enamel well is more desirable than a slight saving in cleaning costs. Such factors, however, as rapidity of production, air costs, ventilating costs, abrasive costs, maintenance costs, handling costs, and working conditions should be given all due consideration. The equipment used with silica sand

abrasive is not usually as efficient with steel grit as one which is selected for that purpose.

Equipment. Blasting equipment can be divided into five groups; (1) the equipment necessary for handling the ware, (2) the ventilating equipment and blasting chamber, (3) the mixing equipment, (4) the equipment necessary for handling and recovery of the abrasive, and (5) that for compressing and distributing the air.

The blasting equipment used in enameling plants varies from the inefficient hand operation methods to the highly efficient automatic blasting machine. The blasting of large irregular shapes such as sanitary ware and castings used for stoves is generally done by an operator, but the equipment is usually quite modern. The old, poorly ventilated and lighted blasting room is rapidly being replaced by the more modern type. Blasting barrels, tables, and conveyor types are being utilized wherever possible. The efficiency of the blasting equipment is to a considerable extent dependent on the *handling of the ware*. The equipment should not be idle longer than necessary while the ware is being moved, therefore, automatic conveyors and turn tables have aided these operations greatly.

The blasting room shown in the diagram of Figure 47 is of the down draft type and is most convenient. The air for *ventilation* enters through the baffles in the roof and proceeds down through the grated floor, carrying the dust and abrasive with it. The booth is lighted by electric bulbs protected with thick glass shades in the ceiling. The doors are so built that maximum sized ware can be wheeled into the booth, or a turn table is built so that one-half is inside and the other outside. The ware to be blasted is placed on the outer shelf of the table while that on the inside is being blasted. The turn table is then turned 180° and the blasting, unloading, and loading resumed. Such an arrangement keeps the blasting in almost constant operation.

The *mixing of the abrasive* with the air is based on either the induction principle or the direct pressure principle.

In the methods using the induction principle, the abrasive may be charged into the gun either by the suction or the gravity method. The gun using the suction method is illustrated in Figure 48. The air escaping rapidly from the air jet creates a suction or reduced pressure in the abrasive inlet. Air from the atmosphere, therefore, is drawn through the abrasive hose carrying the abrasive with it into the mixing chamber of the gun. The abrasive is then picked up by the rapidly flowing air from the air jet and carried rapidly out through the nozzle. The abrasive is usually fed into the abrasive

hose by gravity as illustrated in Figure 49, the atmospheric air passing through the inlets carrying abrasive with it to the gun.

The gravity method differs from the suction method in that the abrasive is fed by gravity directly into the gun in the path of the high pressure air jet. Figure 50 illustrates the general construction of the gravity type of gun. Air is drawn into the mixing chamber

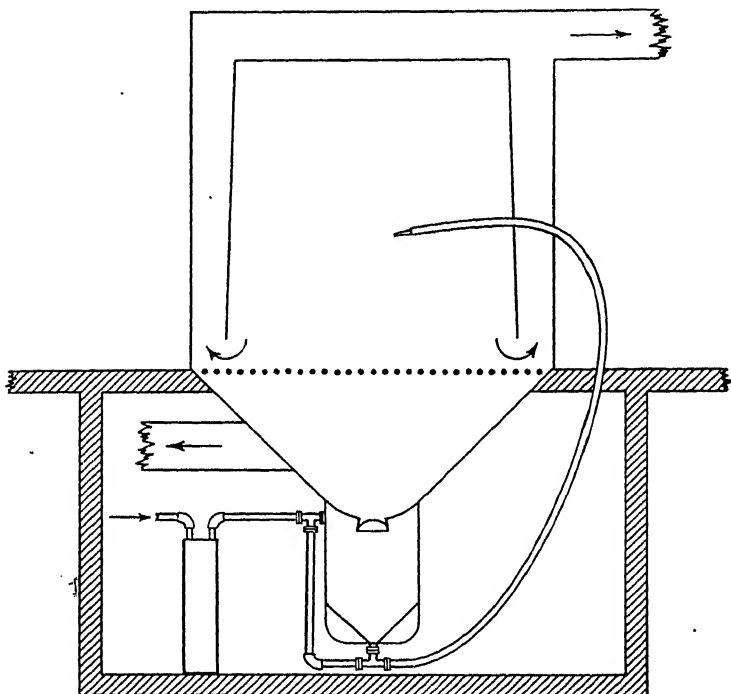


FIGURE 47. Down Draft Blasting Room.

by the reduced pressure created by the high pressure air jet. The abrasive is thereby drawn into the path of this jet and thrown forcibly through the nozzle.

In the direct pressure method the compressed air picks up the abrasive without the use of auxiliary air. This air under pressure then carries the abrasive through the nozzle clear to the tip. This method necessitates a pressure tank, since the supply of abrasive must be under the same pressure as the air blast to permit its injection. Figure 51 shows the principle of the pressure tank with the refilling chamber to permit continuous service.

The pressure in the lower chamber is always at that of the compressed air. The pressure is shut off the upper chamber when filling it, the abrasive flowing through the upper valve from the storage chamber. The upper valve is then closed and compressed air allowed to flow into the upper chamber. In this condition the upper and lower chambers are both at the pressure of the compressed air,

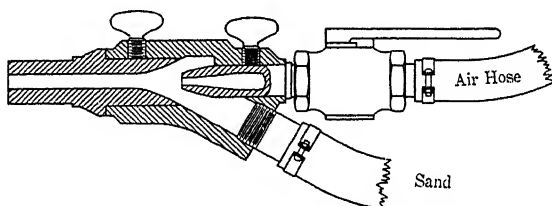


FIGURE 48. Induction Sand Blast Gun.

The lower valve is opened and the abrasive from the upper chamber flows into the lower chamber. The lower valve is then closed and the operation repeated. This can be made entirely automatic or it can be operated by hand.

Abrasive handling can be divided into three methods: gravity, pneumatic, and mechanical.

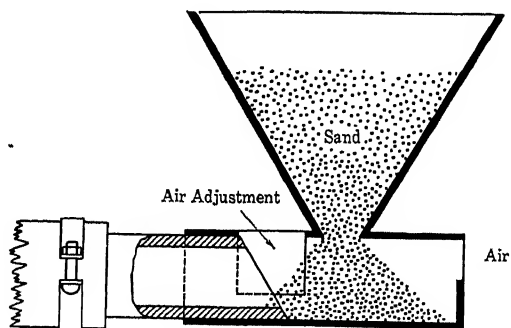


FIGURE 49. Abrasive Feed for Induction Type Gun.

The gravity method is illustrated in Figure 47. In this method, which is the simplest of the three, the abrasive falls through the floor of the booth and is then fed into the pressure tank for re-use. Dust separation is only partially complete as it depends entirely on the ventilation of the room. This results in a considerable quantity of dust in the abrasive and causes a great deal of dust in the booth.

The pneumatic method is illustrated by Figure 52. In this method the dust and sand settle into a hopper under the booth and are then picked up by atmospheric air and exhausted through a vertical tube and dust separator to the dust arrester. The dust separator consists of a series of baffles, the coarse abrasive falling into a chute and the dust passing off with the air to the dust arrester. This method gives good abrasive separation, but it requires high air velocity to raise the abrasive. Sand requires a velocity of approximately 3500 feet

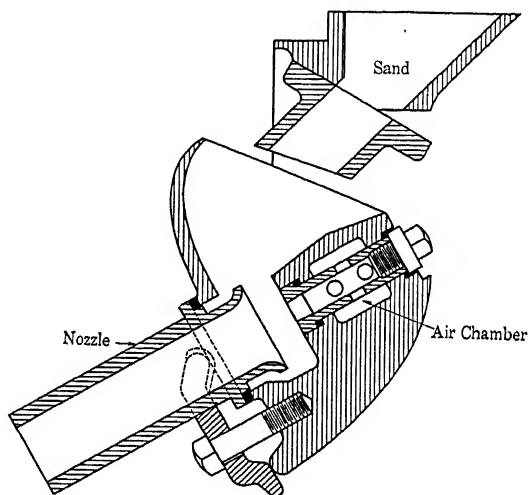


FIGURE 50. Gravity Type Sand Blast Gun.

per minute while steel grit requires about 6000 feet per minute. If, as is often the case with steel grit, a mixture of different sizes is used, then the finest abrasive is lost to the dust arrester if the velocity of the air is high enough to lift the coarser sizes. It is generally conceded that the pneumatic method is wasteful of power and that the separation under these conditions is not accurate enough for greatest efficiency.

Mechanical methods vary considerably in design. Figure 53 illustrates a common design. The abrasive and dust fall through the floor grating of the booth and are then conveyed by means of a screw conveyor to the foot of a bucket elevator. The elevator raises the material to the screens or other separating equipment where the good abrasive is returned to the storage. The dust is discarded, thus relieving the dust arrester of considerable load.

The *compressed air* at the blasting machine should be cool and as free as possible from oil and moisture. When air is compressed it becomes heated and on cooling the moisture is thrown out. In some installations an after cooler is used to eliminate as much as possible of this water, but in most cases sufficient can be eliminated by blow offs and mechanical moisture separators. The mechanical water separator is a cylinder provided with a series of baffles which eliminate a large percentage of the moisture and oil. If the air lines are installed in cool places and all taps are made at the tops

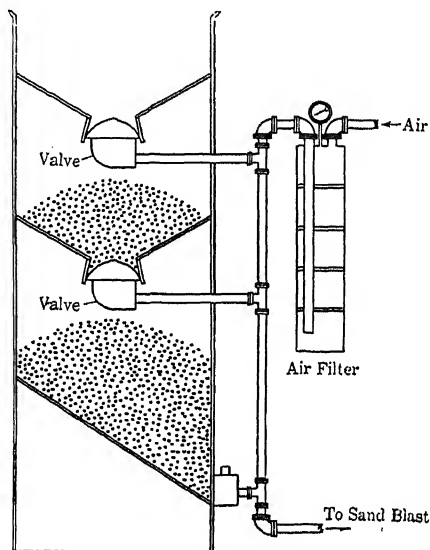


FIGURE 51.

Pressure Tank for Direct Principle Blasting.

considerable trouble can be avoided. The air should not be taken off the end of the line but back from the end where the moisture does not accumulate. All pipes and hose should be of generous sizes to avoid friction and gauges should be installed near the blasting equipment.

Sandblasting has often been a neglected part of the enameling process, from the standpoint of efficiency, the quality of the work, and the health of the workman. Such should not be the case, however, for its results are important to successful operation.

After blasting, the castings should all pass through the finishing and inspection department. Here all rough projections are ground down and the casting is given its final inspection; any slag holes are

punched open and filled, after which the casting is sent to the department for application of the ground coat. After blasting the ware is handled as little as possible and should not stand around any longer than is necessary.

DE-ENAMELING AND REPAIRING

Defective enameled ware is very difficult to repair, often representing a total loss. In sheet metal and wet-process cast iron enamel-

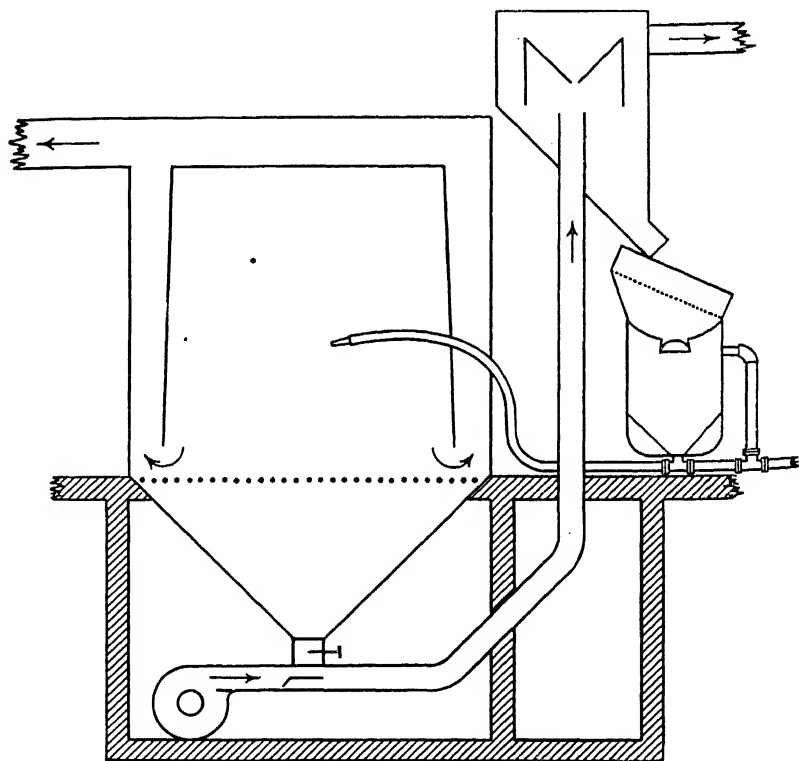


FIGURE 52. Pneumatic Abrasive Handling.

ing an additional coating can be applied to cover black specks, small pin holes, and other minor defects. This requires an extra firing operation, but it is in general the most satisfactory method. The additional coat, however, often slightly changes the whole appearance so that it does not match the general run of ware.

If the defect is fishscaling, blisters too large to be covered, chipping or crazing, the only possible method of recovering the stock is de-

enameling. Dry process cast iron ware cannot be heated after it has once been cooled; therefore any repairing must be done during the firing operation or without heat. Many attempts have been made to use a gun similar to the metal layer gun for applying enamel to the cold ware. This method is only satisfactory where appearance is not important as the patch always shows. It is applicable, however, in the prevention of corrosion. In the manufacture of large pieces of ware, such as bath tubs, it is often possible to grind off a

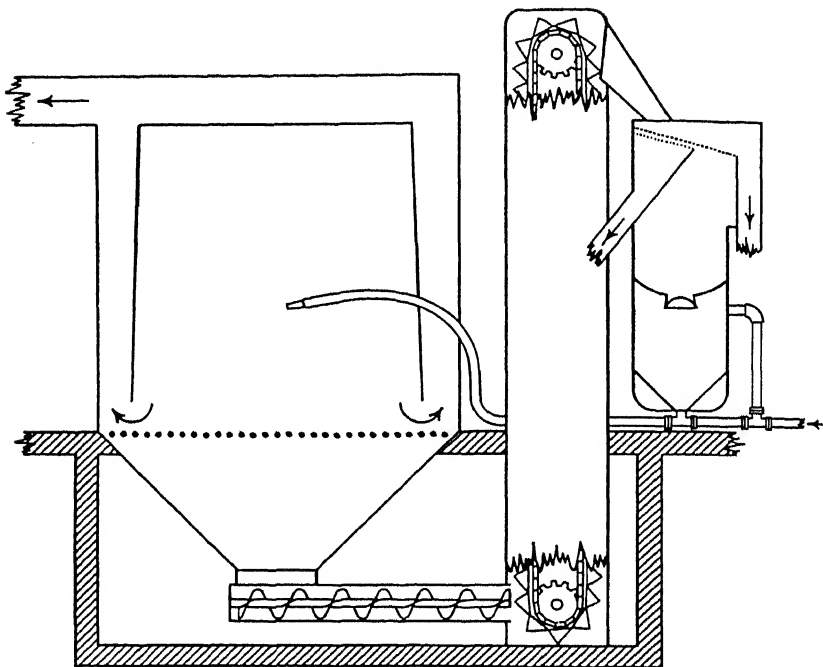


FIGURE 53. Mechanical Abrasive Handling.

surface speck and polish the enamel down, making a very presentable repair. The technique of patching small spots has been highly developed in a few plants, but unless the production is very large it cannot be utilized to full advantage. The objectionable practice of using lacquers and paint enamels for repairing is limited, fortunately, to few places in the industry.

De-enameling is a serious problem, depending greatly on the nature of the enamel being removed. Acid resisting enamels are, in general, very difficult to remove from the metal, while soft soluble enamels are quite easily dissolved off. In the de-enameling of cast iron, sand

blasting is usually resorted to. Higher pressures (80-90 lbs.) are best for sand blasting the enamel off the castings. Such ware, however, is often placed as a back stop for the sand in the cleaning operation, thus utilizing this waste. Enamel is difficult to remove by blasting and requires considerable time. In some plants the castings to be de-enamelled by blasting are first soaked in tanks of waste pickle acid, or alkali solutions to soften the enamel. In other places the enamel is chipped off the ware with a hammer and chisel and then blasted. In any case the de-enameling of castings is expensive and should be avoided by better control in the enamel shop.

The de-enameling of wet-process cast iron and sheet metal ware is often done by solutions. Three methods are possible; the acid method, the alkaline solution method, and the molten caustic method.

The *acid method* employs a variety of acids and procedures. Such acids as sulphuric, chromic, hydrochloric, and hydrofluoric are used. With the exception of hydrofluoric acid, these acids do not remove acid-resisting enamels. Hydrofluoric acid, however, is seldom used as it is expensive, dangerously corrosive, and the fumes are poisonous.

Sulphuric acid is used hot and although it removes soft enamels, its action is slow. The last traces of enamel must be removed by rubbing, scraping, or blasting. Hydrochloric acid (muriatic) in strengths up to twenty per cent is used cold because of the offensive fumes given off by the hot acid. It attacks the iron quite rapidly and is quite expensive. Chromic acid solutions of a forty per cent strength are used hot and will remove some enamels quite satisfactorily. It is very expensive, however, and in the hot condition is very corrosive. In the acid removal of enamel, many hours of treatment are usually required and the last traces of the enamel coating must be removed by other means.

The caustic *alkali solution method* varies with the concentration of the solution and the amount of agitation. In concentrated solutions (about 50% NaOH) heated to three or four hundred degrees Fahrenheit, the action is quite rapid, the enamel coating being removed in a few hours. The use of dilute solutions requires long soaking and has met with little favor. The alkali solutions become loaded with a sludge and soluble silicate salts. This slows down the operation of the bath until it operates so poorly as to be useless. Water must be added to make up for evaporation and the whole bath must be frequently replaced by a new one. The alkali consumption is, therefore, high and the method is fairly expensive.

The *molten caustic method* is the most rapid method of de-enameling. It requires only a few minutes to dissolve enamel off the iron in molten sodium hydroxide at a temperature of about 1000° F. It does not attack iron and is, therefore, used in an iron tank.

To make this method economical, however, the sodium hydroxide which is changed to soluble silicates must be recovered. This can be done by treatment with steam which hydrolyzes the soluble silicates, throwing the silica down as a sludge. The sludge settling on a false bottom must be frequently removed. The ware must be washed and sometimes scrubbed or lightly sand blasted to remove the last adhering scum of oxides which is left.

If enameled iron is treated with steam, solutions, or vapors under pressure, and an accompanying increase of temperature, the enamel is rapidly disintegrated and partially dissolved. This offers some promise as a method for de-enameling.

CHAPTER 6

Enamel Calculations

The representation of enamel compositions and the accompanying calculations are essential to any method of comparison. Enamel compositions may be represented as percentage amounts of the raw materials, percentage amounts of the melted constituents, and as empirical formulæ. Mill additions are generally represented as parts of each material added to one hundred parts of frit. The mill additions are not calculated into the percentage raw materials, but may or may not be calculated into the percentage melted composition or the empirical formula. In some cases, it is desirable to consider the melted composition independently of the mill additions and, in fact, some enamellers prefer to exclude the opacifiers and compare only the melted compositions of the glasses. The coefficient of expansion of an enamel should be calculated from the melted composition, including both opacifiers and mill additions.

THE BATCH COMPOSITION, "BATCH"

The batch composition is a tabulation of the relative amounts of the raw materials entering the enamel mix. It is the method used in representing the amounts of the materials to be weighed in making the enamel batch. In using the batch composition for comparison, the amounts of the different materials should be percentages of the whole batch. To change any batch to per cent batch composition, divide the amount of each material by the sum of all of the materials and multiply by one hundred.

THE MELTED COMPOSITION

The melted composition is a list of the relative amounts of the different constituents present in the frit. For the comparison of different enamel compositions, the melted composition is made to equal one hundred per cent. This can be done by dividing the amount of each constituent by the sum of all of the constituents and multiplying by one hundred. In the smelting of an enamel the raw materials undergo decomposition, oxidation, reduction, and combination, which results in the liberation of certain volatile constituents. This volatilization, involving mainly water and carbon dioxide, results in a loss of from ten to thirty per cent of the raw batch. The melted composition is therefore quite different from the batch composition and, since most of the raw materials have undergone a chemical change, the melted

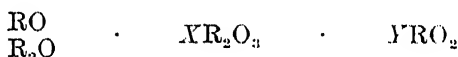
composition is represented in terms of the oxides, elements, or compounds known to be present.

THE CHEMICAL COMPOSITION

The chemical composition may or may not be identical with the melted composition. It is the result of a chemical analysis of the melted enamel and, therefore, is subject to the losses involved in making the enamel.—Some of the fixed oxides, such as soda, boric oxide, and silica, may be volatilized with some of the fluorine. These losses account for the difference between the melted composition and the chemical composition. In the following calculations the melted composition contains all of the fluorine and the fixed oxides, while the chemical composition includes only those constituents actually present.

THE EMPIRICAL FORMULA

The empirical formula is based on the molecular relations existing between the constituents of the melted composition. The sum of all of the basic constituents is made to equal one, so that all formulæ will be calculated to the same basis. A general empirical formula may be given as follows:



The R represents any element and the O represents oxygen. R_2O and RO are general formulæ for basic oxides, such as Na_2O and CaO , R_2O_3 is a general formula for the intermediate oxides, such as Al_2O_3 , and RO_2 is the general formula for the acid oxides, such as SiO_2 .

Examples. The following are examples of the three common methods of representing an enamel composition:

1.	BATCH COMPOSITION	
	<i>Material</i>	<i>Amount</i>
	Feldspar.....	31.0
	Borax.....	31.0
	Quartz.....	20.0
	Soda ash.....	7.0
	Soda nitre.....	3.0
	Fluorspar.....	6.0
	Cobalt oxide.....	0.5
	Manganese dioxide.....	1.5
		<hr/> 100.0

MILL ADDITION

Frit.....	100.0
Clay.....	7.0
Borax.....	0.5

2.

MELTED COMPOSITION

<i>Constituent</i>	<i>Amount</i>
Na ₂ O.....	11.9
K ₂ O.....	6.0
CaO.....	5.0
Al ₂ O ₃	9.8
B ₂ O ₃	13.2
SiO ₂	48.4
CoO.....	0.6
MnO ₂	1.7
F ₂	3.4
	<hr/> 100.0

3.

EMPIRICAL FORMULA *

.582 Na ₂ O			
.135 K ₂ O		.196 Al ₂ O ₃	2.212 SiO ₂
.257 CaO	•	.538 B ₂ O ₃	• .254 F ₂
.021 CoO			.057 MnO ₂
.005 MgO			

THE FACTOR METHODS OF CALCULATION

The enameler in a plant generally compares his enamel compositions on the basis of either the percentage batch composition or the percentage melted composition. These two methods are serviceable, but should be thoroughly understood to avoid misinterpretation. If the compositions being compared are similar, no serious difficulty is encountered, but, if the compositions are quite different, care must be taken.

In using the percentage batch composition, it must be remembered that the frit compositions resulting from very different batch compositions may be similar or quite different. This is due to the fact that the different oxides in an enamel are contributed from various raw materials. For illustration, take the two formulæ which follow; the batch compositions are quite different, but their melted compositions are identical:

* Since manganese produces a pink color in enamels and since the available expansion factors are based on MnO₂, it is assumed to be present as such in these calculations.

BATCH COMPOSITION			MELTED COMPOSITION	
Material	A Amount	B Amount	Constituent	A or B Amount
Feldspar.....	30.00	22.03	Na ₂ O.....	13.87
Borax.....	26.00	22.23	K ₂ O.....	5.96
Quartz.....	20.00	23.68	B ₂ O ₃	11.19
Soda ash.....	8.00	3.56	Al ₂ O ₃	7.30
Soda nitre.....	2.00	5.74	SiO ₂	46.35
Fluorspar.....	6.00	F ₂	5.35
Cryolite.....	3.00	8.00	CaO.....	5.06
Sodium antimonate.....	5.00	Sb ₂ O ₃	4.92
Whiting.....	7.43		
Boric acid.....	1.80		
Antimony oxide.....	3.83		
Pearl ash.....	1.70		
	100.00	100.00		100.00

If these two compositions were compared only on the basis of the batch, one would conclude that the enamels were decidedly different, but, compared on the basis of the melted composition, they would be considered alike. This is an exaggerated example of commonly occurring conditions, which are liable to lead to serious misinterpretation.

If the melted composition alone is used for comparing enamels, we are subject to uncertainty, since the nature of the raw batch may be quite different for one and the same melted composition. The raw materials entering the batch influence the melting of the enamel; they influence the loss of the volatile and fixed oxides, as well as the rate of reaction in forming the glass; and, as a result, they affect the properties of the frit.

It is evident from the above discussion that the comparison of enamel compositions should ordinarily be made on both the raw composition and the melted composition. Where enamels are similar in composition, and where the raw materials do not vary over too wide a range, one mode of comparison is often satisfactory.

In research work, it is often desirable to represent composition in terms of the empirical formula, so as to make comparisons of enamels on a molecular basis. For illustration, it may be desired to express the molecular ratio of the content of bases to that of acids, one type of base to another, intermediate to acid, and so on, in this way studying the relations which may be used to point out the characteristics of the composition.

Since the enameler must be able to convert the batch composition to the melted composition and vice versa, to compare his enamels accurately, it is essential that he have some convenient method of conversion. The method of calculating from the batch composition to the

melted composition and vice versa is comparatively simple and is the particular calculation most used by the enameler. This method of calculation is called the factor method and will be described before going into the more technical discussion of the chemical method, which can be used conveniently for calculating, when tables of factors are not available.

The Calculation from the Batch Composition to the Melted Composition. The raw materials used in making enamels are, in general, of fairly uniform composition. Feldspar, being a rock material, varies most in composition, but, with the greater care in blending and improved control now existing in the chemical industry, a good grade of feldspar will run fairly uniform in composition. A good feldspar should have not only a desirable chemical composition, but it should be mineralogically feldspar without an excessive quartz content. A chemical analysis of the feldspar used is essential to accurate calculations of enamel compositions. The fluorspar, cryolite, and borax compositions should also be checked to insure a uniform supply.

Table 16 gives a list of the raw materials commonly used in enamels. The first column gives the common commercial names of the materials, arranged in alphabetical order, and the second column the empirical formulæ. The remainder of the table is devoted to factors for calculating from the batch composition to the melted composition and vice versa. These factors are divided into five groups, *i.e.*, the basic materials, the intermediate oxides, the acid materials, special materials, and total melted weights for each raw material.

The use of this table can be best illustrated by the calculation of a problem.

Example. Calculate the melted composition from the following batch composition of a sheet iron cover enamel.

<i>Material</i>	RAW BATCH	<i>Amount</i>
Feldspar.....		29
Borax.....		26
Quartz.....		20
Soda ash.....		5
Soda nitre.....		4
Fluorspar.....		5
Cryolite.....		11
<i>Material</i>	MILL ADDITION	<i>Amount</i>
Frit.....		100
Clay.....		7
Tin oxide.....		7
Borax.....		0.5
		<hr/> 114.5

FACTORS FOR CALCULATION

MATERIAL	CHEMICAL FORMULA	BASIO MATERIALS						INTER- MEDIATE OXIDES	ACIDIC MATERIALS			SPECIAL MATERIALS			SPECIALS	LOSS	TOTAL RE- TAIN- ED		
		Na ₂ O	K ₂ O	CaO	MgO	BaO	ZnO	PbO	Al ₂ O ₃	B ₂ O ₃	SiO ₂	TiO ₂	SnO ₂	ZrO ₂				Sb ₂ O ₃	CaF ₂
esia	MgO				[1.000]														1.000
esium carbonate	MgCO ₃				.476														.524 .476
esium hydrate	Mg(OH) ₂				.690														.310 .690
anganese dioxide	MnO ₂														[1.00]	MnO ₂			1.000
al oxide (black)	NiO ₂														.904	NiO		.096	.904
al oxide (gray)	NiO														[1.000]	NiO			1.000
	NaNO ₂	[.365]																	.635 .365
l ash	K ₂ CO ₃		[.681]																.319 .681
esium carbonate	K ₂ CO ₃		[.681]																.319 .681
esium nitrate	KNO ₃		[.465]																.535 .465
lustite	MnO ₃														[1.00]	MnO ₃			
tu	SiO ₂									[1.000]									1.000
lead	Pb ₂ O ₄						[.980]												.020 .980
le	TiO ₂									[1.000]									1.000
nitre	KNO ₃		[.465]																.535 .465
l	SiO ₂									[1.000]									1.000
a	SiO ₂									[1.000]									1.000
ate of soda	Variable																		
ash	Na ₂ CO ₃	[.585]																	.415 .585
um meta antimonate	NaSbO ₃	[.161]											.756			.839	Sb ₂ O ₃		
nitre	NaNO ₂	[.365]																	.635 .365
um siliconfluoride	Na ₂ SiF ₆	[.390]								.319				.447	[.606]				
um silicate	Variable																		
el	Variable																		1.000
oxide	SnO ₂										[1.000]								1.000
zium oxide	TiO ₂										[1.000]								1.000
ting	CaCO ₂			[.560]															.440 .560
te lead	2PbCO ₂ Pb(OH) ₂						[.864]												.136 .864
oxide	ZnO					[1.000]													1.000
onium oxide	ZrO ₂									.075		[.900]							1.000

The use of a chart, such as that illustrated in Table 17, will greatly facilitate calculation. This chart gives a list of the common raw materials used in the batch composition, followed by a series of columns grouped as basic oxides, intermediate oxides, acid materials, special materials, and total weights. The raw materials are arranged with the most common constituents first and the less common ones farther down the list.

The first step, in calculating from the batch composition to the melted composition, is to list the amounts of the different constituents under the heading of batch compositions.

The second step is to calculate the amounts of basic, acidic, intermediate, and special constituents contributed to the enamel by each raw material. This calculation consists of referring to Table 16 and obtaining the factor for each constituent and multiplying it by the amount of the raw material. For example, the amount of feldspar is twenty-nine parts, as given by the batch composition. From Table 16, the factor for the K_2O contributed by feldspar is .169. This factor .169 for K_2O is multiplied by the per cent of feldspar in the raw batch 29, $(.169 \times 29 = 4.9)$, which gives the weight of K_2O contributed to the enamel by the feldspar. This value 4.9 is then placed in the K_2O column opposite feldspar as shown in Table 17. In a similar manner for Al_2O_3 , $.183 \times 29 = 5.3$ parts of Al_2O_3 , and for SiO_2 , $.648 \times 29 = 18.8$ parts of SiO_2 . Since there is practically no loss in melting feldspar, the sum of K_2O (4.9) + Al_2O_3 (5.3) and silica (18.8) equals 29, the amount of the original feldspar.

Each raw material is thus calculated and the chart is filled out as shown†, the mill additions being put in the lower part of the table. The amounts of each constituent in the frit are added together and these sums are then added, which total is the melted weight (83.2). This value should check with the sum of the values in the column marked total retained. The total retained may be computed by adding the sums of each constituent across the chart, or by multiplying each amount in the raw batch by the factor for the total retained as shown by Table 16. The sum of this column is the total retained, or the melted weight.

The sum of the constituents in the frit will not equal one hundred because of the loss during melting; therefore, it is necessary to convert this total to one hundred so that the amounts of each constituent will

† In the case of cryolite, the calculation may be to NaF and AlF_3 or Na_2O , Al_2O_3 and F_2 . Fluorspar may be calculated to CaF_2 or CaO and F_2 . These variations are subject to choice, the author preferring, in general, to calculate to fluorides. This facilitates calculation back to the batch composition.

represent percentages. This is done by dividing the sum for each constituent by the melted weight of the enamel; the sum of the sums of all constituents retained after smelting, or as in the example Table 17 (83.2), and multiplying by 100.

Having brought the melted weight of the frit to 100 per cent, the mill addition can next be considered. It will be noted that the mill addition calls for one hundred parts of frit, seven parts of clay, seven parts of tin oxide and five-tenths parts of borax. Since the mill addition is based on one hundred parts of frit, we can add the melted weights of the mill addition directly to this to obtain the final melted composition of the enamel. Since the sum with the mill additions no longer equals one hundred, it must again be changed to per cent by dividing each constituent by the sum (113.4) and multiplying by 100. If no mill addition is used, it is, of course, unnecessary to continue after calculating the percentage melted weight of the frit.

Factors for Feldspar. The factors for feldspar given in Table 16 are based on a theoretically pure orthoclase feldspar. It will be noticed, on referring to the table, that there are no values given for the commercial feldspars. These spaces are to be filled in with the values for the particular feldspars used in the enamel. The chemical analysis of a feldspar furnishes all of the information necessary to obtain these factors. A commercial feldspar suitable for enamel making might show the following chemical composition on analysis:

FELDSPAR ANALYSIS "A"	
<i>Composition</i>	<i>Per Cent</i>
SiO ₂	69.2
Al ₂ O ₃	17.6
Fe ₂ O ₃	0.1
CaO.....	0.5
K ₂ O.....	9.1
Na ₂ O.....	3.2
Loss on ignition.....	0.3
	<hr/> 100.0

The per cent of each constituent divided by one hundred gives the factor to be used for the particular feldspar. Therefore, in feldspar "A" the factor for K₂O is .091, for Na₂O is .032, for Al₂O₃ is .176, etc.

The Calculation of the Coefficient of Expansion of an Enamel. To calculate the coefficient of expansion of an enamel, it is necessary to represent the composition in terms of the per cent melted composition. Given the enamel in this form, the calculation of its coefficient of

expansion consists of multiplying the per cent of each constituent by a factor for that constituent, Table 2, and taking the sum of the products.

Three sets of factors are given in this table, the oldest set being those of Winkelmann and Schott marked W. and S. The set of factors most commonly used by the enameler is that of Mayer and Havas marked M. and H., while the set of figures by Fetterolf and Parmelee are the most recent values available. For enamel glasses the factors by Mayer and Havas are recommended until others are proved to be more generally applicable.

The chart shown in Table 17 offers a very convenient method of calculating the coefficient of expansion of enamels from their per cent melted weights.

An example is as follows:

MELTED COMPOSITION				
Constituent	Per Cent		M. and H. Factor	Coefficient
Na ₂ O.....	13.9	×	10.	= 139.
K ₂ O.....	4.5	×	8.5	= 38.2
B ₂ O ₃	14.3	×	0.1	= 1.4
Al ₂ O ₃	7.5	×	5.0	= 37.5
SiO ₂	49.9	×	0.8	= 39.9
CaF ₂	7.5	×	2.5	= 18.8
CoO.....	.6	×	4.4	= 2.6
MnO ₂	1.8	×	2.2	= 4.0
100.0		Enamel Coefficient :		281. × 10 ⁻⁴

The calculated coefficient of expansion is not an accurate value for the coefficient of expansion of an enamel, but is merely an approximation to give some basis for comparison. The coefficient of expansion of an enamel can be determined very accurately in the laboratory by using a Pulfrich-Fizeau interferometer.

The Calculation of Enamel Costs. It will be noticed that the chart in Table 17 also provides space for the calculation of costs, which is very convenient and necessary for the plant man. This chart is recommended as a standard form for the calculation of enamels and can be mimeographed on standard letter size paper, 8½ x 11, and easily filed for reference.

The Calculation from the Melted or Chemical Composition to the Batch Composition. The calculation from the melted composition to the batch composition requires judgment and a knowledge of enamels. One must be familiar with the particular type of enamel being calculated and the functions of the raw materials used in the enamel.

If the melted composition includes the mill additions, this must be considered; otherwise erroneous results would be obtained. If the melted composition has been calculated from the batch composition, the conversion back again is not particularly difficult, since the volatilization of different constituents during the smelting does not enter the problem. In a chemical analysis of an enamel, however, it is probable that some of the constituents of the original batch, such as fluorine and boric oxide, may have low values because of volatilization in processing. Since the extent of this volatilization depends on the composition and processing of the enamel, one can only make an estimate as to the probable loss.

To illustrate the calculation of the batch composition from the melted composition the following example of a sheet iron cover enamel is used, the melted composition being as follows:

MELTED COMPOSITION *	
<i>Constituent</i>	<i>Amount</i>
Na ₂ O.....	13.9
K ₂ O.....	5.0
Al ₂ O ₃	10.5
B ₂ O ₃	9.8
SiO ₂	42.5
SnO ₂	6.0
CaO.....	3.7
F ₂	8.6
	100.0

Table 18 illustrates a very convenient method of arranging the calculation. The melted composition of the enamel is inserted on the first line, each constituent being placed under the proper heading.

Since this enamel is a sheet iron cover enamel, it undoubtedly has a mill addition of both clay and an opacifier and probably an electrolyte. Since the electrolyte would be present only in a very small amount, it can be neglected, the amount required to set up the enamel being added as needed after the batch has been calculated.

An ordinary sheet iron cover enamel will contain six or seven per cent of clay; therefore, the first step will be to supply this clay. Opposite the amount of clay we will, therefore, place the figure 6.00. By referring to Table 16, the factors for Al₂O₃ and SiO₂ in clay are .395 and .465, respectively. Since $6 \times .395 = 2.38$, the latter figure

* This problem would be less difficult, if the fluorides were represented as such, but the above is characteristic of a report on the chemical analysis of an enamel.

Enamel—
Batch No.—
Made by—
Date—

[illegible]

is placed opposite clay in the column for Al_2O_3 . Likewise, since $6 \times .465 = 2.79$ of SiO_2 it is placed opposite clay in the column for SiO_2 .

Referring again to the melted composition, it is noted that tin oxide to the amount of six per cent is included and, since this oxide is used only as a mill addition in sheet iron cover enamels, the total amount (6.00) is transferred to the space opposite opacifiers in the SnO_2 column. Under the kind of opacifier (2nd column), we place the formula SnO_2 , and under *the amount* we place the amount of SnO_2 (6.00). This value in the batch is equal to the percentage in the melted composition, for there is no loss on smelting tin oxide.

On again referring to the melted composition, it will be noted that there is probably no other constituent which should be assigned to the mill addition. The next step is the subtraction of the amounts assigned to the mill addition from the original melted composition, the result being placed on the line indicated as the melted composition of the frit.

If the enamel being calculated does not have a mill addition, the original melted weight will be the melted weight of the frit, and, therefore, can be transferred directly to this line in the chart.

To calculate the per cent of the mill addition, divide each amount by the per cent of the melted composition left after these mill additions have been subtracted, and multiply by 100. In this example, subtract 2.38 per cent Al_2O_3 , 2.79 per cent SiO_2 , and 6.00 per cent SnO_2 , leaving 88.8 per cent frit. The per cent of clay equals $6 \times \frac{100}{88.8} = 6.7$ per cent and the per cent of tin oxide $= 6 \times \frac{100}{88.8} = 6.7$ per cent. These values are placed in the column indicating per cent.

To calculate the batch composition for the frit, it is necessary to take the constituents in an order which will make possible a well-balanced batch. If this were not done, it would be necessary to fill out the composition with materials which are rarely used in enamels. The result would be an expensive and an inferior batch, which would probably not have the properties desired, either during fritting or as the frit. The chart in Table 18 gives the most common order of considering the different constituents. Fluorine is commonly contributed to the batch as fluorspar or cryolite or both, although in special compositions other sources of fluorine are sometimes resorted to.

If calcium is present in the composition, it is probably present as fluorspar, therefore we use sufficient fluorine in fluorspar to contribute the lime present. To do this, take the amount of CaO as given by the melted weight and convert it to fluorspar by dividing by the factor given in Table 16 for converting from fluorspar to CaO ($3.70 \div$

.718 = 5.15). This value is then placed in the column *Amt.* on the line for fluorspar. Under the CaO column, opposite fluorspar, place the amount of CaO used, and under the fluorine column opposite the fluorspar place the amount of fluorine used. This is determined by multiplying the amount of fluorspar (5.15) by the factor for fluorine in Table 16 (.487), which gives 2.51 for fluorine. Subtracting these values, we obtain Remainder (1).

On observing Remainder (1) it will be noted that the composition still contains fluorine and, since there is no lime left, this fluorine is logically assigned to cryolite. On dividing this amount of fluorine (6.09) by the factor for converting cryolite to fluorine (.543), the amount of cryolite (11.20) required to furnish this much fluorine is obtained. This value is placed in the *Amt.* column opposite cryolite. Since 6.09 of fluorine is contributed by this cryolite, this value (6.09) is placed in the fluorine column opposite cryolite. The cryolite, however, also contributes alumina, the amount being determined by multiplying the amount of cryolite (11.20) by the factor for Al_2O_3 in cryolite, or .243, which equals 2.72. This value is, therefore, placed in the Al_2O_3 column opposite cryolite. Cryolite also contains sodium, therefore the amount of cryolite (11.20) is also multiplied by the sodium oxide factor (.443), which gives the amount of Na_2O (4.96), which is put in its appropriate space. These values are then subtracted and Remainder (2) obtained.

Since there is no more fluorine present, the next step is a consideration of the constituents K_2O and Al_2O_3 . In general, these are added as feldspar, the amount of feldspar being determined by the alumina content. If this results in not utilizing all of the K_2O , one may either introduce the remainder as pearl ash or consider it equivalent to Na_2O and introduce it as soda ash. The latter method may lead to trouble, if an appreciable amount is substituted. If there is insufficient potash to satisfy this amount of feldspar, it may be desirable to introduce some of the alumina as clay, thereby reducing the amount of feldspar.* A matter of judgment is involved in these cases.

Remainder (2) contains 5.40 parts of Al_2O_3 , which after dividing by the Al_2O_3 factor for feldspar, Table 16, gives $5.4 \div .183 = 29.50$, which is placed in the *Amt.* column opposite feldspar. Using the factors and multiplying by this amount, we obtain the parts of K_2O ($29.50 \times .169 = 5.00$) and SiO_2 ($29.50 \times .648 = 19.11$), which are then, with Al_2O_3 , placed in their appropriate spaces on the chart. A subtraction is then made to obtain Remainder (3).

* Most commercial feldspars contain sodium oxide as well as potassium oxide.

Practically all enamels contain soda nitre; therefore, this is the next constituent to be assigned. We will assume that it is desired to have about four per cent; therefore, that value will be given to the nitre. Using the factor of Table 16, we have $4 \times .365 = 1.46$ of Na_2O used as sodium nitrate. This value is placed in the Na_2O column opposite the soda nitre and a subtraction is again made, giving Remainder (4).

Borax is the next material to be considered, the amount being, if possible, based on the B_2O_3 content of the melt. If this requires too much Na_2O , part of the B_2O_3 will have to be added as boric acid. If this does not use all of the Na_2O , that remaining will be assigned to soda ash. Since there are 9.80 parts of B_2O_3 , we divide this by the factor for converting borax to B_2O_3 and obtain the amount of borax ($9.80 \div .366 = 26.80$). This value is then placed in the *Amt.* column opposite borax, 9.80 is placed in the B_2O_3 column and ($26.80 \times .163 = 4.38$) is placed in the Na_2O column. A subtraction is then made, giving Remainder (5).

Since soda and silica are the only constituents left, the Na_2O is added as soda ash, the amount of soda ash being $3.10 \div .585 = 5.30$, which is placed in its appropriate column. A subtraction is again made to give Remainder (6), which contains only silica. This silica is assigned to quartz and, since quartz is pure silica, the batch and melted amounts are alike. The remainder is then zero.

To change the frit batch to per cent batch composition of the frit, add the amounts of each constituent, divide each constituent by the sum (102.55) and multiply by 100.

The batch formula of this enamel is:

FRIT BATCH	
<i>Material</i>	<i>Amount</i>
Feldspar.....	28.8
Borax.....	26.1
Quartz.....	20.1
Soda ash.....	5.2
Soda nitre.....	3.9
Fluorspar.....	5.0
Cryolite.....	10.9
	<u>100.0</u>

MILL ADDITION	
<i>Material</i>	<i>Amount</i>
Frit.....	100.0
Clay.....	6.7
Tin oxide.....	6.7
	<u>113.4</u>

Although some of the steps in this calculation are arbitrary or are subject to the judgment of the calculator, it shows the general method which may be modified slightly to fit any case in hand.

Calculation of the Empirical Formula from the Melted or Chemical Composition and Vice Versa. The factor method of calculating from the melted composition to the formula and vice versa is essentially the same as the chemical method, therefore the reader is referred to page 143, in which the chemical method for this calculation is described.

Substitution. The enameler often wishes to modify his formula without making extensive changes. In such cases substitution is resorted to, as in the use of sodium antimonate to furnish the antimony instead of antimony oxide, and the use of cryolite to furnish the fluorine in place of fluorspar. An example will show the calculation necessary in such a substitution. Given the following sheet iron cover enamel, sodium antimonate will be substituted for the antimony oxide.

<i>Material</i>	<i>Amount</i>
Feldspar.....	26
Borax.....	24
Quartz.....	18
Soda ash.....	10
Soda nitre.....	4
Fluorspar.....	5
Cryolite.....	8
Antimony oxide.....	5
	<hr/>
	100

The amount of sodium antimonate necessary to furnish five parts of antimony oxide is first determined by dividing by the factor for Sb_2O_3 in NaSbO_3 in Table 16, thus: $5 \div .756 = 6.61$.

To determine the amount of sodium oxide in the sodium antimonate, multiply the amount of sodium antimonate (6.61) by the factor for sodium oxide in sodium antimonate (.161), which gives 1.06. This sodium oxide added in sodium antimonate must be subtracted from some other source of sodium in the batch to avoid changing the chemical composition of the enamel. Since soda ash is present in a considerable amount, it is the logical substitution. The parts of Na_2O $(1.06) \div .585 = 1.81$. The 1.81 parts of soda ash are then subtracted from the ten parts of soda ash called for by the formula $(10 - 1.81 = 8.19)$.

The new formula with the substitution of sodium antimonate as a source of antimony for the antimony oxide is then changed to 100 per cent and appears as follows:

<i>Materials</i>	<i>Original Composition</i>	<i>New Composition</i>	<i>New Per Cent Composition</i>
Feldspar.....	26	26.	26.1
Borax.....	24	24.	24.1
Quartz.....	18	18.	18.0
Soda ash.....	10 — 1.81 =	8.19	8.2
Soda nitre.....	4	4.	4.0
Fluorspar.....	5	5.	5.0
Cryolite.....	8	8.	8.0
Antimony oxide.....	5 substitute NaSbO ₃	6.61	6.6
	100	99.80	100.0

THE CHEMICAL METHOD OF CALCULATION

Although the chemical method of calculation requires more knowledge of chemistry than the factor method, it does not require an extensive knowledge. It is more flexible than the factor method, and is often used in research and other laboratory work. This method is similar to the Norm method used for the calculation of minerals and mineral aggregates. It might well be called the molecular method, for, although it does not assume that the units are molecules, it treats them as though they were. It is based on formula or equivalent weights.

In the chemical method of calculation, all materials are considered to be made up of oxides, rather than of the elements used in pure chemistry. Fluorine and fluorine compounds, however, are exceptions and are considered as such.

The oxides may be divided into three groups: the acid oxides, the basic oxides, and the intermediate oxides. The basic oxides have the general empirical formula R_2O or RO , the intermediate oxides R_2O_3 , and the acid oxides RO_2 , where R represents any element and O represents oxygen.

The ordinary oxides occurring in enamels are included in the following classification:

BASES R_2O or RO	INTERMEDIATES R_2O_3	ACIDS RO_2
Sodium oxide..... CaO	Aluminum oxide..... Al_2O_3	Silicon dioxide..... SiO_2
Potassium oxide..... MnO	Boric oxide..... B_2O_3	Titanium oxide..... TiO_2
Calcium oxide..... BaO	Ferric oxide..... Fe_2O_3	Zirconium oxide..... ZrO_2
Magnesium oxide..... K_2O	Antimony oxide..... Sb_2O_3	Manganese dioxide... MnO_2
Barium oxide..... Na_2O	Chromic oxide..... Cr_2O_3	
Zinc oxide..... MgO		
Ferrous oxide..... ZnO		
Manganous oxide.... FeO		
Lead oxide..... PbO		
Cobalt oxide..... CoO		

In the chemical analysis of raw materials and products the results are generally expressed in terms of the oxides most likely to be present. A chemical analysis of a feldspar, for example, will appear as follows:

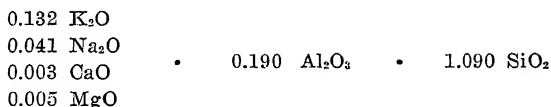
FELDSPAR ANALYSIS	
<i>Composition</i>	<i>Amount</i>
SiO ₂	65.58
Al ₂ O ₃	19.36
CaO.....	0.16
MgO.....	0.20
K ₂ O.....	12.44
Na ₂ O.....	2.56

The Calculation of the Empirical Formula from the Melted or Chemical Composition. The method of calculation from the melted composition or the chemical composition to the empirical formula is identical*

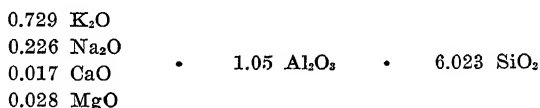
To calculate the empirical formula from the melted composition, the amount of each constituent is divided by the equivalent weight † of each oxide, the resulting values being termed *equivalents*. The following example shows such a calculation for a feldspar:

EXAMPLE					
<i>Constituent</i>	<i>Amount</i>		<i>Equivalent Weight</i>		<i>Equivalents</i>
SiO ₂	65.58	÷	60.1	=	1.091
Al ₂ O ₃	19.36	÷	101.9	=	0.190
CaO.....	0.16	÷	56.1	=	0.003
MgO.....	0.20	÷	40.3	=	0.005
K ₂ O.....	12.44	÷	94.2	=	0.132
Na ₂ O.....	2.56	÷	62.0	=	0.041

The second step in the calculation consists in the arrangement of the oxides in the form of the empirical formula, thus:



The RO group is then calculated to a total of 1.000. This is done by adding the equivalents of the RO group and dividing the equivalents of each of the oxides in the formula by this sum. These values arranged as a formula constitute the empirical formula of the feldspar:



* If the melted composition is calculated, it may differ from the results of a chemical analysis, because some of the enamel constituents may be lost in smelting and firing.

† The equivalent weights of the oxides are given in Table 62 of the appendix.

Although the values would be different in calculating an enamel, the procedure is the same as that for a feldspar.

The Calculation of the Formula Weight. The formula weight is calculated by multiplying the number of equivalents of each constituent in the empirical formula by the equivalent weights of the particular constituents. The sum of these products is the formula weight.

EXAMPLE

<i>Empirical Formula</i>		<i>Equivalent Weight</i>		
0.729 K ₂ O	×	94.2	=	68.6
0.226 Na ₂ O	×	62.0	=	14.0
0.017 CaO	×	56.1	=	1.0
0.028 MgO	×	40.3	=	1.1
1.050 Al ₂ O ₃	×	101.9	=	107.0
6.023 SiO ₂	×	60.1	=	362.0
Formula Weight =				<u>553.7</u>

The formula weight would be the equivalent weight and molecular weight of a material, if the empirical formula were the actual molecular formula of the material. For the purpose of calculation it is used as though it were the molecular weight and it is called the formula weight to avoid the misuse of the term molecular weight.

The Calculation of the Melted or Chemical Composition from the Empirical Formula. The calculation of the chemical composition from the empirical formula consists of two steps. First, we multiply the equivalents of each constituent in the formula by its equivalent weight; secondly, we add these products and change to per cent by dividing each by the sum and multiplying by 100.

Example. Taking the formula of an enamel and arranging the equivalents in tabular form, the following illustrates the calculation

.582 Na ₂ O			
.135 K ₂ O			
.257 CaO	.	.196 Al ₂ O ₃	2.212 SiO ₂
.005 MgO		.538 B ₂ O ₃	.057 MnO ₂
.021 CoO			.254 F ₂

of the melted composition:

<i>Constituents</i>	<i>Equivalents</i>		<i>Equivalent Weight</i>		<i>Relative Amount</i>	<i>Per Cent Composition</i>
Na ₂ O.....	.582	×	62.0	=	36.08	13.37
K ₂ O.....	.135	×	94.2	=	12.72	4.72
CaO.....	.257	×	56.1	=	14.42	5.34
MgO.....	.005	×	40.3	=	.20	.07
CoO.....	.021	×	74.9	=	1.57	.58
Al ₂ O ₃196	×	101.9	=	19.97	7.40
B ₂ O ₃538	×	69.6	=	37.45	13.87
SiO ₂	2.212	×	60.1	=	132.94	49.25
MnO ₂057	×	86.9	=	4.95	1.83
F ₂254	×	38.0	=	9.65	3.57
				Sum	<u>269.95</u>	<u>100.0</u>

The Calculation of the Batch Composition from the Melted or Chemical Composition. It is often desired to calculate the batch composition from the chemical analysis of an enamel. This calculation requires a knowledge of enamels and good judgment, since there are many possible batch compositions which could be obtained from the same chemical composition. If one has a knowledge of the type of enamel used, he can closely approximate the batch composition, but there is no way of being absolutely sure. A chemical analysis does not give a very good indication of the volatile substances which the batch contains, and, therefore, it leaves this to the experience and judgment of the calculator.

The following example will illustrate the calculation of a sheet iron ground coat batch composition from the chemical analysis.†

Example. The chemical analysis of a sheet iron ground coat is as follows:

<i>Constituents</i>	<i>Amount</i>
Na ₂ O.....	13.37
K ₂ O.....	4.74
CaO.....	5.34
MgO.....	.07
Al ₂ O ₃	9.79
B ₂ O ₃	13.86
SiO ₂	52.04
F ₂	3.57
CoO.....	.58
MnO ₂	1.83
Sum.....	105.19

The first step in the calculation is that of converting the amount of each constituent into equivalents by dividing each by its equivalent weight as follows:

<i>Constituents</i>	<i>Amount</i>		<i>Equivalent Weight</i>		<i>Equivalents</i>
Na ₂ O.....	13.37	÷	62.	=	.2156
K ₂ O.....	4.74	÷	94.2	=	.0504
CaO.....	5.34	÷	56.1	=	.0952
MgO.....	.07	÷	40.3	=	.0017
Al ₂ O ₃	9.79	÷	101.9	=	.0961
B ₂ O ₃	13.86	÷	69.6	=	.1992
SiO ₂	52.04	÷	60.1	=	.8663
F ₂	3.57	÷	38.0	=	.0940
CoO.....	.58	÷	74.9	=	.0077
MnO ₂	1.83	÷	86.9	=	.0211

† The chemical composition from analysis would be the same as the calculated melted composition, if no loss of fixed oxides or fluorine occurred during smelting.

After the equivalents for each constituent have been calculated, they are tabulated as shown in Table 19. This method of tabulation greatly facilitates calculation and is very convenient.

At this point one must inspect the situation carefully. In the present example, for illustration, one is dealing with a sheet iron ground coat; therefore it is necessary to consider the mill addition first. The mill addition of most ground coats consists of six or seven per cent of clay and a very low percentage of electrolyte. Since the amount of electrolyte is very small, it is usually neglected, but the clay must be considered. Clay has the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; therefore it contributes both Al_2O_3 and SiO_2 to the melted composition. If we take .0234 equivalent of clay, which in the present problem will result in about six per cent of clay in the mill addition, it will contribute .0234 equivalent of Al_2O_3 and $2 \times .0234 = .0468$ equivalent of SiO_2 to the enamel. Twice as many equivalents of SiO_2 as Al_2O_3 are contributed, because of the fact that there are two equivalents of SiO_2 in the clay molecule and only one equivalent of Al_2O_3 . The number of equivalents of clay (.0234) is placed in the column headed Batch Equivalents, and under the composition on the same line with the words, Clay (Mill). The amounts of Al_2O_3 and SiO_2 (.0234 and .0468 respectively) are placed opposite clay in their appropriate columns, as shown in Table 19. The equivalents of Al_2O_3 and SiO_2 contributed by the clay are then subtracted from the enamel composition and the first remainder is obtained.

In general, after disposing of the materials entering the mill batch, it is a good plan to assign the oxides which can be obtained from only one material, that material furnishing only one oxide. These can all be handled in one subtraction. In the present example we have two; CoO , which can be added as Co_3O_4 , and MnO_2 , which is added as MnO_2 , as shown in Table 19. Since there are three CoO equivalents in one Co_3O_4 , only one-third as many equivalents of Co_3O_4 (.0026) are required as CoO equivalents (.0077). The MnO_2 is added in the number of equivalents required (.0211). After placing these in the appropriate columns, another subtraction is made and the second remainder is obtained.

The fluorine compounds are the next logical constituents to be disposed of. Since this is a sheet iron ground coat, it is not likely to contain cryolite, and since it does contain CaO , this calcium should be assigned to fluorspar, thus using all of the fluorine shown by the chemical analysis. It will be noted that there are more equivalents of CaO (.0952) than there are of F_2 (.0940), which indicates that the

TABLE 19
THE CALCULATION OF THE BATCH COMPOSITION FROM THE MELTED COMPOSITION USING EQUIVALENTS.

Composition	Batch Equivalent	Na_2O	K_2O	CaO	MgO	Al_2O_3	B_2O_3	SiO_2	F_2	CoO	MnO_2
Enamel.....	S.S.G.	.2156	.0504	.0952	.0017	.0961	.1992	.8663	.0940	.0077	.0211
Clay (Mill).....	.023402340468
First Remainder.....		.2156	.0504	.0952	.0017	.0727	.1992	.8195	.0940	.0077	.0211
Cobalt oxide.....	.00260077
Manganese oxide.....	.02110211
Second Remainder.....		.2156	.0504	.0952	.0017	.0727	.1992	.8195	.0940
Fluorspar.....	.094009400940
Third Remainder.....		.2156	.0504	.0012	.0017	.0727	.1992	.8195
Feldspar.....	.0692	.0156	.0504	.0012	.0019	.07274170
Fourth Remainder.....		.20001992	.4025
Borax.....	.09961992
Fifth Remainder.....		.10044025
Soda nitre.....	.0446	.0223
Sixth Remainder.....		.07814025
Soda ash.....	.0781
Quartz.....	.40254025
Seventh Remainder.....	

S.S.G. = Sheet steel ground cont.

fluorine content is either low or CaO is contributed from some other source. Whiting is not commonly used in a sheet iron ground coat, and especially not in such a small amount as to furnish this CaO (.0012 equivalent). On referring to the feldspar formula, page 143, it is noted that the feldspar contributes a small amount of CaO, therefore it is logical to assume that this .0012 equivalent of CaO is contributed by feldspar. In ordinary calculations this small amount of CaO might be neglected, but, as shown in the present example, it is actually taken care of by the feldspar.

On calculating a batch from an actual chemical analysis, the fluorine is usually lower than would be expected from the composition of the raw materials, because some of the fluorine is lost in smelting and firing. In calculating under such conditions, the amount of fluorine lost must be estimated and introduced in the calculation. The amount of CaO often indicates the amount of fluorine which should be present, as in the present example of a sheet iron ground coat the CaO is practically all contributed as fluorspar with no cryolite present. Such conditions make the calculation of a batch from a chemical analysis uncertain.

Returning to the example, the fluorine (.0940 equivalent) is all calculated to fluorspar (.0940 equivalent) requiring .0940 equivalent of CaO. These amounts are placed in their appropriate columns of Table 19, a subtraction is made, and the third remainder is obtained.

Since the alumina is not added as cryolite and since the mill addition of clay has already been taken care of, the only other logical addition of this oxide is as feldspar. Clay is not usually added in the frit, because it is desirable to use as much feldspar as the Al_2O_3 will permit, the feldspar being a cheap source of the alkalies.

In the third remainder, there is .0727 equivalent of Al_2O_3 , which is assigned to feldspar, the amounts of the various constituents contributed by the feldspar being placed in their appropriate columns opposite feldspar. In the feldspar being used, the formula on page 143 shows 1.05 equivalents of Al_2O_3 and, since .0727 equivalent of Al_2O_3 is required for the enamel, only $.0727 \div 1.05$ or .0692 equivalent of feldspar is used. The amount of feldspar (.0692) is placed in the Batch Equivalents column and the amount of Al_2O_3 (.0727) is placed in the Al_2O_3 column, Table 19. This amount of feldspar also contributes .0692 times the equivalents of Na_2O , K_2O , CaO, MgO, and SiO_2 , indicated by the feldspar formula. If the CaO and MgO are very small, they may be neglected, but they are considered in this example. The

number of equivalents of each oxide is placed in its column, and a subtraction made, which gives the fourth remainder.

The fourth remainder contains Na_2O , B_2O_3 , and SiO_2 . The B_2O_3 is assigned to borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, which contributes Na_2O as well as B_2O_3 . Since there are two molecules of B_2O_3 in the borax molecule, only one-half as many equivalents of borax are required as B_2O_3 equivalents, to satisfy the composition ($.1992 \div 2 = .0996$); therefore .0996 equivalent of borax is added, which, in turn, contributes .0996 equivalent of Na_2O . After placing these values in the appropriate columns, another subtraction is made and the fifth remainder is obtained.

Only about one-fourth of the remaining Na_2O is assigned to soda nitre, which is practically always present, but only in small amounts (3-5%). Since one molecule of soda nitre (NaNO_3) contains only one-half an equivalent of Na_2O , twice as many equivalents of NaNO_3 must be used to furnish a given number of equivalents of Na_2O . If .0223 equivalent of Na_2O is to be contributed by NaNO_3 , .0446 equivalent of NaNO_3 is required. These values are placed in the table and another subtraction made, giving the sixth remainder.

The remaining Na_2O is assigned to soda ash (Na_2CO_3) and the SiO_2 is assigned to quartz. The final subtraction of these two, results in the seventh remainder, which equals zero.

The batch composition has now been obtained in terms of equivalents as shown by the column headed Batch Equivalents in Table 19. To change these equivalents to weights, multiply each by its equivalent or formula weight. Add the products of the frit constituents and divide each product by the sum. Multiply by 100, to obtain the per cent batch composition of the frit.

<i>Materials</i>	<i>Batch Equivalents</i>		<i>Equivalent (Formula) Weight</i>		<i>Batch</i>	<i>Per Cent Frit Batch</i>
Clay.....	.0234	×	258.0	=	6.04
Cobalt oxide.....	.0026	×	240.8	=	.63	0.51
Manganese dioxide.....	.0211	×	86.9	=	1.83	1.50
Fluorspar.....	.0940	×	78.1	=	7.34	6.00
Feldspar.....	.0692	×	553.7	=	38.32	31.31
Borax.....	.0996	×	381.4	=	37.99	31.04
Soda nitre.....	.0446	×	85.0	=	3.79	3.10
Soda ash.....	.0781	×	106.0	=	8.28	6.77
Quartz.....	.4025	×	60.1	=	24.19	19.77
Sum					122.37	100.00

To obtain the per cent clay to be added as a mill addition, the amount of clay (6.04) is divided by the melted weight 122.37 and mul-

multiplied by 100. In the present case the value can be taken directly, but if the melted weight were other than 100, the calculation would be necessary.

The amount of clay added to 100 parts of frit in the mill is

$$\frac{6.04}{100} \times 100 = 6.04$$

The batch composition of the enamel, arranged in the customary manner, is as follows:

FRIT BATCH	
Feldspar.....	31.3
Borax.....	31.0
Quartz.....	19.8
Fluorspar.....	6.0
Soda nitre.....	3.1
Soda ash.....	6.8
Cobalt oxide.....	.5
Manganese dioxide.....	1.5
	<hr/>
	100.0
MILL BATCH	
Frit.....	100.0
Clay.....	6.04

The amount of water and electrolyte depends upon the kind of clay used, the kind of electrolyte, the condition of the slip, and the properties desired.*

The Calculation of the Melted Composition from the Batch Composition. This calculation does not depend upon the experience or judgment of the calculator, because there is only one melted composition for a given batch composition. The mode of representation sometimes differs from one person to another, because some prefer to represent the fluorine as fluorine, while others represent it as fluorspar, cryolite, or sodium fluoride and aluminum fluoride. There are advantages in each mode of representation. It has been proved that cryolite does not exist in an enamel as such, but that fluorspar does exist in some enamels as calcium fluoride. It is quite probable that the composition of an enamel greatly influences the amounts of the fluorine compounds when such exist. Although the presence of the fluorine compounds is not always certain, it remains that a melted composition, represented so that fluorine is present as the compounds of decomposition compounds of the form in which it was added, does indicate the source of the fluorine. Antimony may be present in the finished enamel as any one or more of its oxides Sb_2O_3 , Sb_2O_4 , and Sb_2O_5 . It

* This is explained and described on page 253.

has been shown that in certain opaque enamels it is present as Sb_2O_3 , but in its dissolved condition it is usually assumed to be present as Sb_2O_3 .

In the calculation of the chemical composition from the batch composition of an enamel, the amounts of the frit batch are converted to per cent by adding the frit batch constituents, dividing each by the sum and multiplying by 100.

Example. The following sheet iron ground coat will be calculated from the batch composition to the melted composition, including the mill addition.

FRT BATCH	
<i>Materials</i>	<i>Amount</i>
Feldspar.....	31
Borax.....	31
Quartz.....	20
Soda ash.....	7
Soda nitre.....	3
Fluorspar.....	6
Manganese dioxide.....	1.5
Cobalt oxide.....	0.5
	100.0

MILL BATCH	
<i>Materials</i>	<i>Amount</i>
Frit.....	100.0
Clay.....	6.
Water.....	43.
Borax.....	0.3

The first step of the calculation is the conversion of the amounts of each constituent to equivalents. This is accomplished by dividing the amount of each constituent by its equivalent or formula weight, as follows:

FRT BATCH				Equivalent (Formula) Weight		Equivalents	
<i>Materials</i>	<i>Amount</i>						
Feldspar.....	31.	÷	553.7	=		.0560	
Borax.....	31.	÷	381.4	=		.0812	
Quartz.....	20.	÷	60.1	=		.3326	
Soda ash.....	7.	÷	106.0	=		.0660	
Soda nitre.....	3.	÷	85.0	=		.0353	
Fluorspar.....	6.	÷	78.1	=		.0769	
Manganese dioxide.....	1.5	÷	86.9	=		.0173	
Cobalt oxide.....	0.5	÷	240.8	=		.0021	

The equivalents are next tabulated as in Table 20. This is a most convenient method of arranging the figures for calculation.

1. Referring to the formula of the feldspar used in the batch, page 143, multiply the number of equivalents of each oxide in the formula by the number of equivalents of feldspar used, and insert in Table 20.

<i>Constituents</i>	<i>Equivalents in Feldspar</i>		<i>Equivalents of Feldspar</i>		<i>Equivalents Used</i>
Na ₂ O.....	.226	×	.0560	=	.0126
K ₂ O.....	.729	×	.0560	=	.0408
CaO.....	.017	×	.0560	=	.0009
MgO.....	.028	×	.0560	=	.0016
Al ₂ O ₃	1.05	×	.0560	=	.0588
SiO ₂	6.023	×	.0560	=	.3375

2. The borax molecule Na₂B₄O₇ · 10H₂O contributes one equivalent of Na₂O for each equivalent of borax and two equivalents of B₂O₃ for each equivalent of borax. Thus, if .0812 equivalent of borax is added, we obtain .0812 equivalent of Na₂O and 2 × .0812, or .1624, equivalent of B₂O₃. These are placed as shown in Table 20.

3. Quartz contributes only SiO₂, giving the same number of equivalents as were introduced.

4. Soda ash contributes one equivalent of Na₂O for each equivalent of Na₂CO₃ added.

5. Soda nitre contributes only one-half as many Na₂O equivalents as sodium nitrate equivalents added, since there is only one-half of an equivalent of Na₂O in one sodium nitrate molecule.

6. Fluorspar contributes one equivalent of CaO and one equivalent of F₂, or one equivalent of CaF₂ for each equivalent of CaF₂ added.

7. Manganese dioxide remains as MnO₂ and, therefore, the equivalents used can be transferred directly to the appropriate column in the table.

8. Cobalt oxide is added as Co₃O₄; it, therefore, contributes three CoO equivalents for each equivalent of Co₃O₄ added.

The totals for each constituent are next determined by adding the vertical columns. These totals represent the number of equivalents of each oxide and of fluorine. To change these to weights, multiply each by its equivalent weight, and then change to per cent by adding the products and dividing each by this sum and multiplying by 100.

TABLE 20
THE CALCULATION OF THE MELTED COMPOSITION FROM THE BATCH COMPOSITION USING EQUIVALENTS

<i>Composition</i>	<i>Batch Equivalent</i>	<i>Na₂O</i>	<i>K₂O</i>	<i>CaO</i>	<i>MgO</i>	<i>Al₂O₃</i>	<i>B₂O₃</i>	<i>SiO₂</i>	<i>MnO₂</i>	<i>CoO</i>	<i>CaF₂</i>
Feldspar.....	.0560	.0126	.0408	.0009	.0016	.05883375
Borax.....	.08121624
Quartz.....	.33263226
Soda ash.....	.0660
Soda nitre.....	.0353	.0177
Fluorspar.....	.07690769
Manganese dioxide.....	.01730173
Cobalt oxide.....	.00210063
Sum.....		.1775	.0408	.0009	.0016	.0588	.1624	.6601	.0173	.0063	.0769

<i>Constituent</i>	<i>Equivalent</i>		<i>Equivalent Weight</i>		<i>Amount</i>	<i>Per Cent Frit</i>
Na ₂ O.....	.1775	×	62.0	=	11.01	13.78
K ₂ O.....	.0408	×	94.2	=	3.84	4.81
CaO.....	.0009	×	56.1	=	.05	.06
MgO.....	.0016	×	40.3	=	.06	.07
Al ₂ O ₃0588	×	101.9	=	6.00	7.51
B ₂ O ₃1624	×	69.6	=	11.30	14.15
SiO ₂6601	×	60.1	=	39.66	49.63
MnO ₂0173	×	86.9	=	1.50	1.88
CoO.....	.0063	×	74.9	=	.47	.59
CaF ₂0769	×	78.1	=	6.01	7.52
			Sum	=	79.90	100.00

After calculating the per cent frit composition the mill additions must be considered. Since the mill addition calls for six parts of clay to one hundred parts of frit, the amounts of Al₂O₃ and SiO₂ added to the enamel by this amount of clay must be determined and added to the per cents of Al₂O₃ and SiO₂ in the frit composition to give the composition of the complete enamel. Their values are then changed to per cent by adding them together and dividing each by the sum and multiplying by 100. The electrolyte is neglected.

To calculate the amounts of Al₂O₃ and SiO₂ in six parts of clay, divide the amount 6 by the formula weight of clay 258, which changes it to equivalents ($6 \div 258 = .0232$ equivalent of clay). The empirical formula for clay, Al₂O₃ · 2SiO₂ · 2H₂O, shows it to contain one equivalent of Al₂O₃ and two equivalents of SiO₂ for each equivalent of clay; therefore, .0232 equivalent of clay furnishes to the enamel .0232 equivalent of Al₂O₃ and $2 \times .0232 = .0464$ equivalent of SiO₂. To change these to weights, multiply each by its equivalent weight as follows:

<i>Constituent</i>	<i>Equivalent</i>		<i>Equivalent Weight</i>		<i>Amount</i>
Al ₂ O ₃0232	×	101.9	=	2.37
SiO ₂0464	×	60.1	=	2.79

These values are added to the per cent frit composition. Since the sum does not then equal 100, the total composition is changed to per cent by dividing each constituent by the sum and multiplying by 100.

<i>Frit Constituent</i>	<i>Amount</i>	<i>Mill Addition</i>		<i>Enamel Constituent</i>	<i>Per Cent Enamel Constituent</i>
Na ₂ O.....	13.78		=	13.78	13.10
K ₂ O.....	4.81		=	4.81	4.57
CaO.....	.06		=	.06	.06
MgO.....	.07		=	.07	.07
Al ₂ O ₃	7.51	+ 2.37	=	9.88	9.40
B ₂ O ₃	14.15		=	14.15	13.45
SiO ₂	49.63	+ 2.79	=	52.42	49.86
MnO ₂	1.88		=	1.88	1.78
CoO.....	.59		=	.59	.56
CaF ₂	7.52		=	7.52	7.15
		Sum	=	105.16	100.00

Substitution. Substitution by the chemical method is quite similar to that of the factor method, except that equivalents are used. Take the example of substituting sodium antimonate for antimony oxide in the batch composition of a sheet iron cover enamel.

<i>Material</i>	<i>Amount</i>
Feldspar.....	26
Borax.....	24
Quartz.....	18
Soda ash.....	10
Soda nitre.....	4
Fluorspar.....	5
Cryolite.....	8
Antimony oxide.....	5
	<hr/> 100

Again the first step is to determine the amount of sodium antimonate necessary to furnish five parts of antimony oxide. To do this, divide the amount of antimony oxide, 5, by its equivalent weight, 291.5, which gives the number of equivalents, .01715. Since sodium antimonate, NaSbO_3 , contains only one-half as many equivalents of Sb_2O_3 as does the antimony oxide Sb_2O_3 , twice as many equivalents are necessary ($2 \times .01715 = .0343$). By multiplying the number of equivalents of sodium antimonate (.0343) by the equivalent weight of sodium antimonate, 192.8, (Table 62) the number of parts of sodium antimonate to be added is obtained: $.0343 \times 192.8 = 6.61$.

However, .0343 equivalent of sodium antimonate NaSbO_3 contains one-half as many equivalents of sodium oxide, Na_2O , and is equivalent to the sodium in one-half as many equivalents of soda, Na_2CO_3 . Then, to compensate for the sodium oxide added as sodium antimonate, one-half as many equivalents of soda ash as sodium antimonate must be subtracted from the soda ash of the original formula. To do this $.0343 \text{ equivalent} \div 2 = .01715 \text{ equivalent of soda ash}$ and on multiplying by the equivalent weight of soda ash ($.01715 \times 106 = 1.81$), the parts of soda ash to be subtracted from that in the original formula are obtained.

The substitution is then applied as follows:

<i>Material</i>	<i>Original Composition</i>	<i>New Composition</i>	<i>Per Cent New Composition</i>
Feldspar.....	26	26	26.1
Borax.....	24	24	24.1
Quartz.....	18	18	18.0
Soda ash.....	10 — 1.81	8.19	8.2
Soda nitre.....	4	4	4.0
Fluorspar.....	5	5	5.0
Cryolite.....	8	8	8.0
Antimony oxide.....	5 substitute NaSbO ₃	6.61	6.6
		99.80	100.0

THE USE OF CHARTS TO FACILITATE THE CALCULATIONS

Where there is considerable calculation to do, it is often convenient to construct charts for this purpose.* These charts, if drawn on a fairly large scale, are quite accurate, but most of those published are too small to be depended upon.

By plotting raw materials on the vertical axis and equivalents on the horizontal axis, with diagonal lines indicating the relations between these two values for the different materials, the most useful type of chart is obtained. Figure 54 illustrates such a chart.

The relative amounts of the raw materials (batch composition) are located on the vertical axis, from which one projects across the chart to the intersection with the appropriate diagonal. From this intersection, drop down to the base line and read off the equivalents of the constituents desired. It then remains only to bring the RO group to equal unity and the formula is obtained.

An example of the use of the chart is as follows:

ENAMEL BATCH COMPOSITION

<i>Materials</i>	<i>Formula</i>	<i>Amount (lbs.)</i>
Feldspar.....	K ₂ O · Al ₂ O ₃ · 6SiO ₂	170
Borax.....	Na ₂ O · 2B ₂ O ₃ · 10H ₂ O	150
Quartz.....	SiO ₂	100
Soda ash.....	Na ₂ CO ₃	40
Soda nitre.....	NaNO ₃	10
Cryolite.....	Na ₃ AlF ₆	30
		500

To obtain the relative equivalents of K₂O and Al₂O₃ in feldspar, Figure 54, locate 170 on the left hand vertical axis, project over to the feldspar diagonal, and from the intersection drop down to the base line which indicates .31 equivalents of K₂O and Al₂O₃. Next project over from 170 to the feldspar-silica diagonal and again drop down to

get the equivalents of SiO_2 , which are 1.84. If, as in this case, the diagonal for feldspar-silica does not intersect the 170 horizontal, take half of 170, or 85, as the horizontal, project over to the intersection and drop down to the base line to obtain .92 as the equivalents which must then be multiplied by 2 which equals 1.84.

The other materials are handled in a similar way and tabulated as follows:

Material	Amount	Constituents					
		Na_2O	K_2O	Al_2O_3	B_2O_3	SiO_2	F_2
Feldspar.....	17031	.31	1.84
Borax.....	150	.3979
Quartz.....	100	1.66
Soda ash.....	40	.38
Soda nitre.....	10	.06
Cryolite.....	30	.210743
		RO	R_2O_3	RO_3			
		1.04 Na_2O	.38 Al_2O_3	3.50 SiO_2			
		.31 K_2O	.79 B_2O_3	.43 F_2			

Divide the equivalents of each constituent by the sum of the RO equivalents (1.35) and arrange the empirical formula as follows:

.77 Na_2O	.28 Al_2O_3	2.59 SiO_2
.23 K_2O	.58 B_2O_3	.32 F_2

Although a fair degree of accuracy is shown here, a larger chart is necessary. Such a chart can be easily constructed by calculating one point for each diagonal and drawing a line through this point and the zero point at the lower left hand corner. To obtain this point divide the amount of the raw material by the equivalent weight, which gives the number of equivalents of the constituent desired.

Other charts may also be found useful, such as one for the conversion from batch or formula composition to melted composition and vice versa. These are constructed in a similar manner.

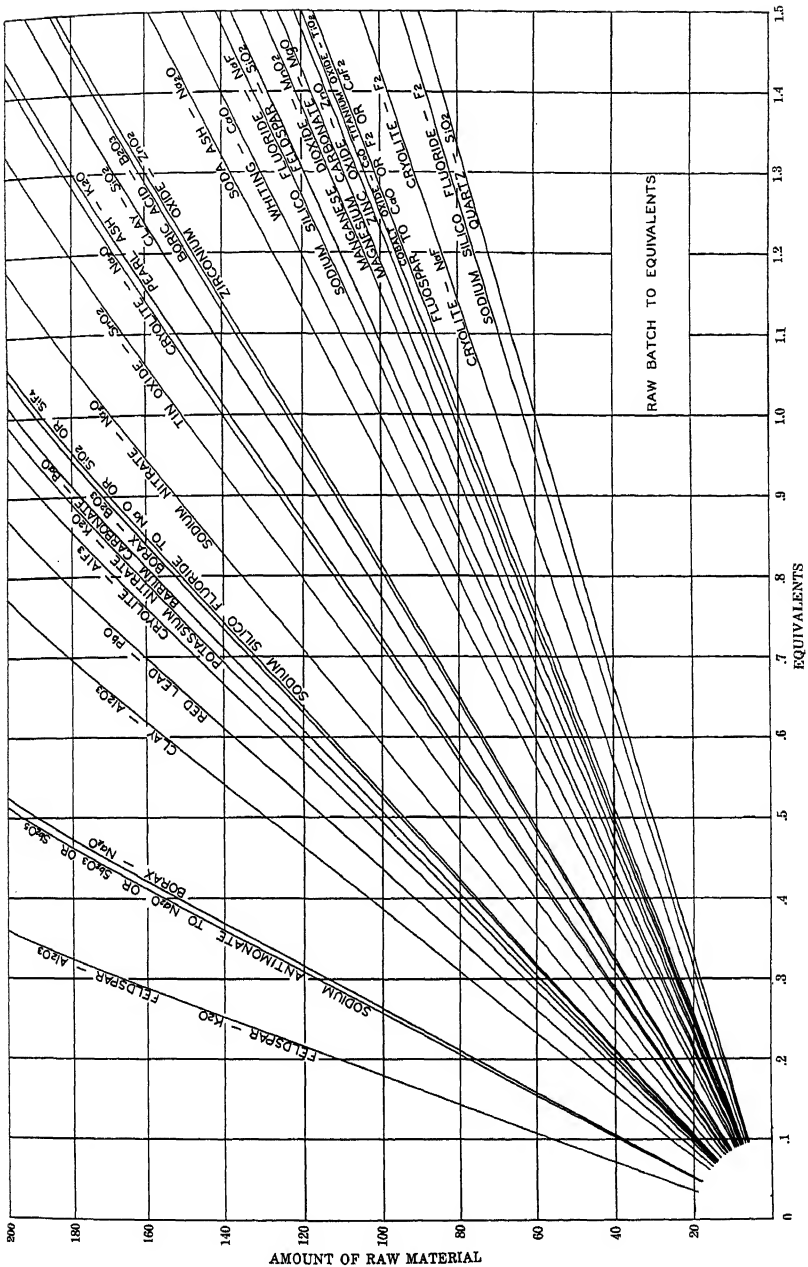
Large, accurately drawn charts are very convenient, not only for straight calculations but also for substitutions in a composition.

In a similar manner, the calculation from batch to melted composition and vice versa can be facilitated. The chart shown in Figure 55 is for this purpose, and it is used in the same manner as the chart in Figure 54. In this case, however, it is suggested that the figures in Table 16 be used to lay out the calculation. The chart merely serves to replace Table 16 in the regular factor method of calculation.

The chart shown in Figure 56 can be used for calculating from the

melted composition to the formula, since it serves to convert melted weights to equivalents.

If charts are to be used for calculation, it is recommended that they be accurately drawn on a 2 x 2 foot surface so as to give the accuracy desired in calculating enamels. Such a chart should be made in one piece, mounted on a stiff board, the accuracy not being sacrificed for convenience in folding or handling.



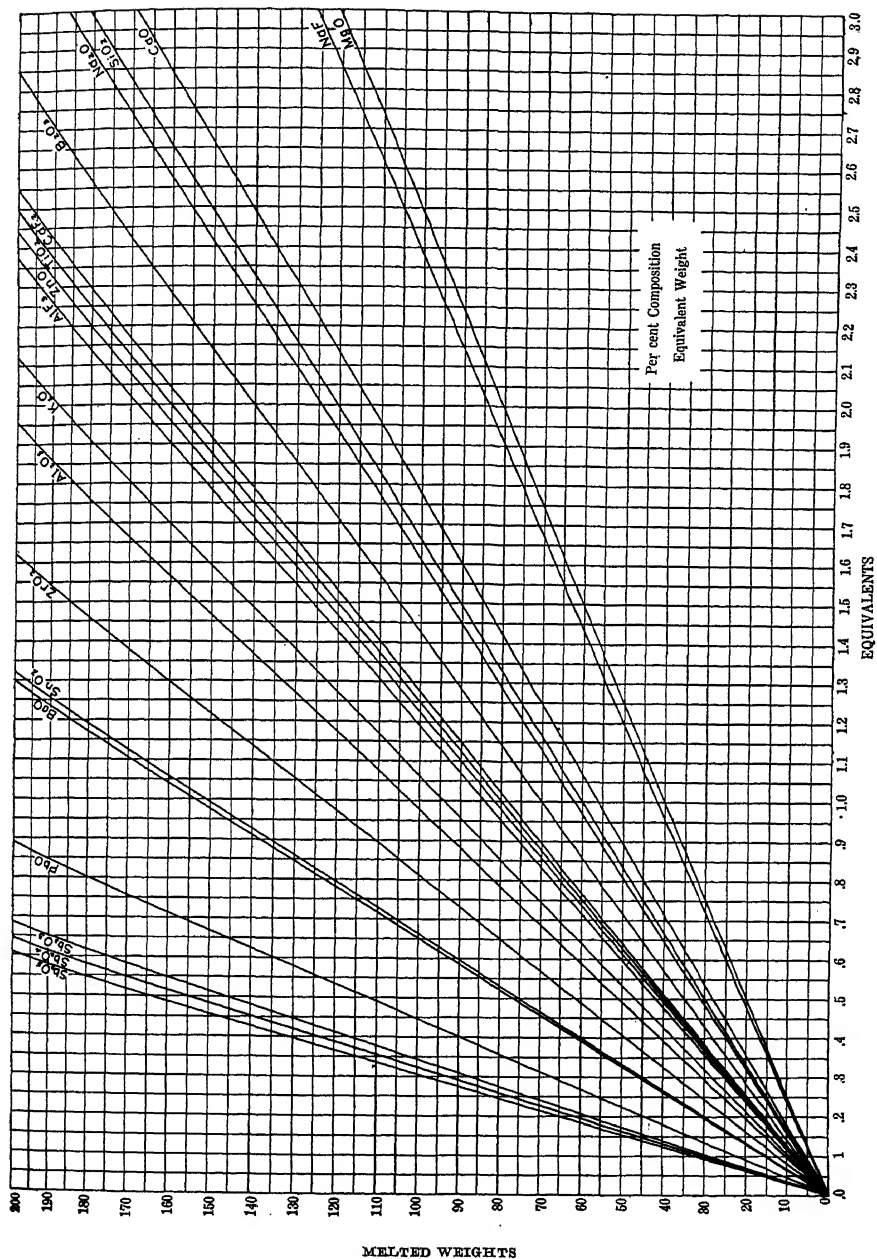


FIGURE 56. Curves for Conversion of Melted Composition to Equivalents.

CHAPTER 7

Enamel Compositions

The common classification of enamels divides them into four large groups as follows: (a) Sheet iron or steel enamels, (b) Dry process cast iron enamels, (c) Wet process cast iron enamels, and (d) Jewelry enamels. Although it is possible to use some cast iron enamels on sheet iron and some sheet iron enamels on cast iron, this practice is not common. An enamel is usually designed for a particular use in which it gives the most satisfactory service. This classification into the four groups is natural as it is convenient both in the industry and in the laboratory.

CLASSIFICATION OF ENAMEL COMPOSITIONS

Sheet Iron or Steel Enamels. Sheet iron or steel enamels are enamels applied to sheet iron or steel. Most of the enameling sheet stock is a low carbon iron, steel being used only where considerable strength is required.

Sheet iron enamels may be further classified as follows:

1. Ground coats
 - (a) Cobalt ground coats
 - (b) Light-colored ground coats
2. White cover coats
 - (a) Soft cover enamels
 - (b) Acid-resisting cover enamels
3. Colored enamels
 - (a) Colored frits
 - (b) Glazes
4. Miscellaneous enamels
 - (a) Beading enamels
 - (b) Decalcomania
 - (c) Graining enamels
 - (d) Mottled enamels

Dry Process Cast Iron Enamels. Dry process cast iron enamels are enamels used in the powder method of enameling cast iron. In this process the iron casting is coated with a refractory first coat and heated, whereupon the cover enamel is applied to the hot ware by dusting it through sieves. Dry process enameling is particularly suitable for heavy castings which require a considerable time to come up to temperature.

Dry process cast iron enamels can be classified as follows :

1. Ground coats (slush coats) (grip coats)
 - (a) Sintered ground coats
 - (b) Glassy ground coats
2. White cover enamels
 - (a) Tin enamels
 - (1) Leadless
 - (2) Low-lead
 - (3) High-lead
 - (b) Antimony enamels
 - (1) Leadless
 - (2) Low-lead
 - (3) Medium-lead
 - (c) Acid-resisting enamels
3. Colored enamels
 - (a) Colored frits
 - (b) Glazes

Wet Process Cast Iron Enamels. Wet process cast iron enamels are the most difficult enamels to use. They are particularly suitable for use on light-weight castings and are very fusible.

Wet process cast iron enamels can be classified as follows :

1. Ground coats
2. White cover enamels
 - (a) Leadless
 - (b) Low lead
 - (c) High lead
3. Colored cover enamels
 - (a) Colored frits
 - (b) Glazes

Jewelry Enamels. The so-called jewelry enamels cover a highly specialized field of enameling. Jewelry enamels are of the type used on bronze, brass, copper, and the precious metals. /

Jewelry enamels may be classified as follows :

1. Enamels used on precious metals
2. Copper enamels

ENAMEL COMPOSITIONS

The composition of an enamel is complicated both by the number of elements which it contains and also the varied source of these elements. It is a glass formed by the fusion, solution, and reaction of a number of raw materials. An enamel is an under-cooled solution, but in addition it holds in suspension color oxides, opacifiers, and gases. It might be considered to be a solid emulsion or suspension, since the color and opacity are due in many cases to the dispersion of these materials throughout the matrix of glass. These opacifying or color particles are

so small that they cannot be seen with a high-powered microscope. Some are crystals produced on cooling the glass, others are caused by the dispersion of solid particles in the molten glass, and still others are probably due to immiscible melts dispersed in the molten material. Enamel glasses are, therefore, not unlike water solutions, suspensions, or emulsions. There is positive evidence that they are subject to the same general laws as other systems of this type. As clay is suspended in water, so the opacifiers are suspended in the glass. It is highly probable that electrolytes play an important part in the dispersion of these opacifiers, just as they affect the dispersion in a clay slip.

^ Since many factors influence the enamel constitution, a chemical analysis gives only part of the information. Chemical changes take place in the formation of enamel glasses, but it is doubtful if these reactions are ever complete in ordinary enamel manufacture. It is quite probable that, were these reactions complete, the enamel would not remain vitreous (glassy), but would devitrify (crystallize), in which case the ultimate constitution would be indicated by the crystals formed. The organic chemist does not consider that an ultimate analysis gives complete information, and neither should the ceramist or enamel chemist.

• When the enamel is applied to the iron and fired, it is changed both chemically and physically. Consider for example the sheet iron cobalt ground coat. In this enamel there are many evident changes during application and firing. In drying, the water evaporates from the enamel, carrying the soluble salts to the surface and concentrating them there. The iron rusts, and some of this rust is absorbed by the enamel, as is often evidenced by the discoloration. During the firing this iron oxide (rust) changes from the red to the black oxide. The iron is further oxidized and a scaly layer forms between the enamel and the iron. With further heating this black oxide scale disappears, probably going into solution in the enamel. The cobalt blue color of the enamel fades as the firing proceeds and a light green shade, characteristic of iron-bearing glasses, takes its place. The gases in the enamel and those formed at the interface slowly escape through the molten enamel until finally the glass settles down to a smooth surface. These are complicated changes, affecting not only the physical condition of the enamel, but also its chemical composition.

^ All ground coats undergo similar changes and, on firing cover enamels, volatilization, decomposition, solution, and reaction with the ground coat contribute to the physical and chemical changes of both the ground coat and the cover enamel.

In smelting enamel batches violent changes take place, as described in Chapter 8. Composition is controlled through this process, to a limited extent, but given a definite composition, as a frit, there are many operations in the working of the enamel which have a decided effect on the physical and chemical properties of the finished enamel ware.

The chemical composition of an enamel is, however, largely controlled by means of the raw batch of the unsmelted enamel. Its characteristics in smelting, milling, applying, and firing must be considered in compounding the batch. There are so many factors which influence the enamel after the batch is actually weighed out accurately; however, that great care must be exercised to obtain a uniform product. These considerations explain, largely, why an enamel working well in one plant often does not prove satisfactory in another. If conditions were identical, it would work the same in both plants.

It is evident, on considering these factors in the making of a successful enamel, that a good batch formula is only one step and not a solution of the difficulties in the making of a good enameled product. Many good enamel formulæ will be found in the pages of this book, but care and patience must be used in the introduction of any new enamel composition into the routine of a plant.

'SHEET IRON OR STEEL ENAMELS'

Sheet iron enamels are usually designed to fire at temperatures between 1500 and 1600° F in a few minutes on 18 to 22-gauge iron. The gauge of the metal stock, however, influences the firing time; therefore very heavy gauge ware may require thirty minutes or even more. When the enamels are designed to fire below 1500° F, they are usually quite soluble and cannot, therefore, be used on all kinds of ware. If the enamels fire above 1600° F, warping of the iron is usually encountered. Where heavy stock is used, the enamels may be fired at somewhat higher temperatures. The thickness of the stock, the shape of the piece, and the thickness of the enamel coating are factors which must be considered in firing any enamel.

SHEET IRON GROUND COATS

Sheet iron or sheet steel enamels require a special ground coat to give the proper adherence of the enamel. Although there are white and gray ground coats, the cobalt blue ground coat is still far more common in plant practice than any other type. It has long been the dream of the enameler to make white or specially colored sheet iron

ground coats, but only in a few cases have they been found economically successful. A discussion of these special types will follow the discussion of the cobalt ground coat.

A good ground coat is essential to the successful enameling of sheet iron. This ground coat must melt down smooth, it must have a wide firing range, and it must not copper-head, blister, fishscale, tear, craze, or chip. Although most ground coats have a good gloss, this is not necessary.

The Cobalt Ground Coat. Since the cobalt ground coat is a cobalt glass, it is blue in color, unless the blue is masked by some other color oxide, such as an oxide of manganese, iron, nickel, or copper. These latter oxides darken the cobalt blue and, if added in large quantities, approach black.*

It is common practice in cobalt ground coats to replace part of the cobalt oxide by the cheaper nickel and manganese oxides. Several times as much of these latter oxides are required, however, to replace a given amount of cobalt oxide. The cobalt oxide cannot be entirely replaced by these oxides without reducing the adherence of the enamel to the metal, but their use in conjunction with cobalt oxide is considered good practice.

- Theory of Adherence. Although many theories have been proposed to explain why the cobalt oxide makes the ground coat adhere to sheet iron and steel, none has been accepted as satisfactory because of their being based on too limited data.

Grünwald advanced the theory that the coefficient of expansion of the enamel was brought close to that of the iron by the addition of cobalt and other metallic oxides. This theory has recently been supported by the work of A. Dietzel and K. Meures,¹ who show that the cobalt increases the solution of the iron in the enamel, the iron thereby raising the coefficient of thermal expansion. These authors believe that through this solution of iron a gradual decrease of the difference of thermal expansion exists between the enamel-iron inter-face and the surface of the enamel. This gradual decrease is believed necessary to prevent rupture during the expansion and contraction of the enameled iron.

Tostman² suggested the cobalt steel alloy theory, namely, that the cobalt oxide is reduced to cobalt which alloys with the iron. The enamel was believed to adhere tenaciously to this alloy. The loss of blue color

¹ Translation by R. M. King, J. Am. Ceram. Soc., February Meeting (1934).

² C. Tostman, Function of Ground Enamels, Keram. Rund. 19, 5 (1911).

on firing seems to favor this theory. Up to the present time no one has been able to prove or disprove it.

Mayer and Havas,³ and Vondracek⁴ advanced the theory that cobalt silicate is formed with the evolution of oxygen. This reaction was believed to clean the iron, making possible the intimate contact between the enamel and the iron.

Berndt⁵ claimed that the oxygen liberated by the iron oxide is fixed by the cobalt oxide, preventing the excessive bubble formation in the enamel, thereby resulting in a stronger structure and better adherence.

Vielhaber⁶ added to this theory of Berndt, stating that the cobalt oxide saturated the enamel to such an extent that the iron oxide did not dissolve in it. He believed that the enamel adhered to the iron oxide layer.

Cooke⁷ presented a somewhat similar theory, in which he believed the inter-facial layer was partially enamel and iron. This layer was assumed to be rich in iron on the enamel side and rich in enamel on the iron side, thus improving the adherence of the enamel to the steel.

Clauson⁸ concluded from a series of experiments that the adherence of the cobalt ground coat was caused by the ability of the cobalt glass to penetrate the pores of the steel and actually etch its way to a good contact.

R. M. King⁹ disagrees with several of the foregoing theories and believes that the adherence is related to the formation of metallic dendrites, which from X-ray investigations appear to be alpha iron. These dendrites form a layer between the enamel and the iron, sometimes projecting quite far into the enamel layer. In this manner they aid the adherence. It was shown that enamels which adhere have this dendritic formation and those which do not adhere do not have it.

³ M. Mayer and B. Havas, Function of Ground Enamel, *Sprechsaal*, 43, 737 (1910).

⁴ R. Vondracek, Function of Ground Enamel, *Sprechsaal*, 44, 15 (1911).

⁵ M. Berndt, Role of Cobalt in a Ground Coat for Sheet-Steel Enamels, *Keram. Rund.*, 22, 262 (1924).

⁶ L. Vielhaber, Behavior of Metal Oxides in Ground Coats on Sheet Steel, *Keram. Rund.*, 33, 53 (1925).

⁷ R. D. Cooke, The Effect of Furnace Atmospheres on the Firing of Enamel, *J. Am. Ceram. Soc.*, 7, 277 (1924), and Making and Firing of Sheet Steel Ground Coats, *J. Am. Ceram. Soc.*, 10, 454 (1927).

⁸ C. D. Clauson, A Study of Adherence of Ground Coats to Sheet Steel, *Cer. Ind.*, 13, 164 (1929).

⁹ Papers on Mechanics of Enamel Adherence: (a) J. O. Lord and W. C. Rueckel, I, *Jour. Amer. Ceram. Soc.* 14 (10) 777-81 (1931); W. C. Rueckel and R. M. King, II, *ibid.*, pp. 782-88; W. K. Carter and R. M. King, III, *ibid.*, pp. 788-94. (b) A. McK. Greaves-Walker and R. M. King, IV, *ibid.*, 15 (9) 476-80 (1932); G. H. Spencer-Strong and R. M. King, V, *ibid.*, pp. 480-83; K. Schwartzwalder and R. M. King, VI, *ibid.*, pp. 483-86; G. H. Spencer-Strong, J. O. Lord, and R. M. King, VII, *ibid.*, pp. 487-90. (c) R. M. King, VIII, *ibid.*, 16 (5) 232-38 (1933). *Jour. Amer. Ceram. Soc.*, 15 (9) 488 (1932).

Staley¹⁰ believes that the dendrites observed by King are metallic cobalt and has shown that plating of certain metals below iron in the electromotive series does exist. Staley's conclusions are:

All the metals between iron and copper in the electromotive-force series of metals, if dissolved in glasses, are plated out of solution, when the glasses are fired as sheet-steel ground coats, by the electrolytic action of the hot iron base.

Of these plates cobalt, nickel, and antimony promote adhesion, each of the following factors probably playing a part:

(1) The plates of these metals adhere tenaciously to steel, while enamel does not.

(2) The coefficients of thermal expansion of these metals are intermediate between those of steel and those of commercial ground-coat and cover-coat glasses, thus giving a gradation of coefficients found desirable by Danielson and Sweely.

(3) The enamel glass is mechanically bonded to the metal plate by dendrites, aided by any jagged projections and holes.

(4) Since these metal plates are insoluble in the molten enamel, any structure favorable to adhesion, once formed, remains.

• It is interesting, in this regard, that rust in contact with the metal base disappears on firing the enamel, but it does not disappear if the rust is suspended in the enamel and is not in contact with the iron. This observation might suggest that the iron oxide is reduced by the iron to a lower oxide which is soluble in the enamel. The elements associated with this phenomenon, iron, cobalt, nickel, and manganese are closely associated with each other in Mendeleeff's Periodic Table of the elements. These elements, therefore, have similar physical and chemical properties.

No theory has been accepted generally as explaining the function of cobalt in sheet iron ground coats, but recent progress has been rapid. It is quite probable that the true explanation will involve several of these theories. Whatever the chemistry of the phenomenon is, the fact remains that small amounts of cobalt oxide produce good adherence where a lack of it results in poor adherence.

• **Cobalt Ground Coat Compositions.** The general composition of cobalt sheet iron ground coats is not particularly complicated, as compared with other enamels. After comparing and studying a great many ground coat compositions, the writer plotted a field of compositions which includes practically all of them.

Table 21 shows the batch compositions and the chemical compositions of twenty-four sheet iron ground coats. The five columns, at the right in Table 21 show the maximum, minimum, average, median, and range for each constituent. Along the bottom of each table the sums of the feldspar, borax, and quartz are given for each enamel.

¹⁰ H. F. Staley, *J. Am. Ceram. Soc.*, 17, 163-7 (1934).

The sums of the feldspar, borax, and quartz for the different enamels have a maximum of about 92 per cent and a minimum of about 75 per cent with an average of 82 per cent. On observation, it will be noted that most of the ground coats have about 82 per cent for the sum of these three constituents. Very few fall outside of the range 76 to 83 per cent.

On further analysis of this table, it is noted that there are few constituents present, other than the feldspar, quartz, and borax. Soda ash and soda nitre together average about eleven per cent and seldom vary far from this value. The fluorspar varies infrequently from four to six per cent. From experience, it seems doubtful if the cobalt oxide need ever vary greatly from the average of 0.5 per cent, or the manganese dioxide far from its average of 1.5 per cent. Taking these values, a general batch can be considered to be as follows:

c Feldspar	}	
Borax		
Quartz		82
Soda ash.....		7
Soda nitre.....		4
Fluorspar.....		5
Cobalt oxide.....		0.5
Manganese dioxide.....		1.5
		<hr/>
		100.0

Although these values can be varied somewhat, and good enamels obtained, the above might well be considered a base formula upon which all others could be built.

To simplify this batch further, it is necessary to study the relative amounts of feldspar, borax, and quartz which are permissible. This can be admirably done by resorting to Table 1, and plotting the results on a triaxial diagram.

The maximum and minimum feldspar are plotted on the diagram, Figure 57. The shaded portions show the fields of compositions not likely to give good enamels.

The maximum and minimum borax are plotted on the diagram in Figure 58. The shaded portion again shows the fields of compositions not likely to give good enamels.

The maximum and minimum for quartz are plotted on the diagram in Figure 59. Again the shaded portion shows the fields of compositions not likely to give good enamels.

Figure 60 shows a diagram of Figures 57, 58, and 59 superimposed

TABLE 21. SHEET IRON GROUND COAT COMPOSITIONS
BATCH COMPOSITION

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	61	29A	29B	10	1	22	18A	18B	180	62	81B	65A	65B	650	65D
Feldspar	23.8	30.0	38.0	36.3	31.2	30.9	22.0	27.0	20.5	29.0	36.4	33.3	28.0	31.0	33.5
Borax	33.3	30.0	26.0	35.6	28.5	25.2	30.0	30.0	39.5	32.0	35.5	36.2	32.0	43.8	37.0
Quartz	21.9	20.0	11.2	14.6	20.0	19.6	29.0	29.0	22.5	19.0	14.4	19.2	20.0	17.0	19.2
Soda ash		7.0	9.0	7.4	9.0	6.4	5.0	9.8	5.0	9.0	7.4	4.5	6.0	3.0	5.6
Soda nitrate	11.4	5.0	3.0		4.0	5.0	4.6	5.0	4.7	5.0		2.2	2.0	1.0	
Fluorspar	4.2	6.0	7.0	5.3	6.0	7.5	6.0	6.0	6.0	4.7	4.6	3.7	3.0	4.0	3.9
Cryolite															
Red lead													8.3		
Whiting			2.0												
Barium carbonate			2.0												
Clay	3.9						0.4	0.5	0.4	0.8	1.0	0.3	0.2	0.1	0.3
Cobalt oxide	0.4	0.5	0.3	0.2	0.3	0.4									
Manganese dioxide	0.7	1.5	0.7	0.6	1.0	5.0	2.0	1.2	1.0	0.5	0.7	0.6	0.5	0.1	0.5
Nickel oxide	0.4		0.2				1.0		0.4						
Copper oxide			0.6												
'aldspar + Borax + Quartz	79.0	80.0	75.2	86.5	79.7	75.7	81.0	77.5	82.5	80.0	86.3	88.7	80.0	91.8	89.7

MELTED COMPOSITION

Potassium and Sodium oxide	17.8	19.9	21.0	20.2	20.7	18.1	16.3	21.7	19.0	22.0	20.3	18.8	17.4	18.7	18.7
Boric oxide	16.0	13.8	11.8	16.3	13.0	11.1	13.6	14.0	19.0	15.0	16.2	16.6	13.4	20.6	16.9
Alumina	7.7	6.9	8.7	8.3	7.1	6.9	5.0	6.2	5.0	6.8	8.3	7.6	7.2	7.4	7.6
Slitica	51.1	49.4	44.4	47.6	50.1	48.1	53.5	48.4	46.8	48.5	47.4	51.2	47.2	47.9	50.9
Calcium fluoride	5.5	7.5	8.7	6.6	7.6	9.1	7.4	7.6	7.9	6.1	5.7	4.6	3.7	5.2	4.9
Barium fluoride			2.0												
Cobalt oxide	0.5	0.6	0.4	0.2	0.4	0.5	0.5	0.6	0.5	1.0	1.2	0.4	0.3	0.1	0.4
Manganese oxide	0.9	1.9	0.9	0.8	1.2	6.1	2.5	1.5	1.3	0.6	0.9	0.8	0.6	0.1	0.6
Nickel oxide	0.5		0.2		1.2		1.2		0.5				(PbO		
Copper oxide			0.7										10.0)		
Calcium oxide			1.2												
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
alkal + Boric oxide + Silic.	89.9	83.1	77.2	84.1	83.9	77.3	83.4	84.1	84.8	85.5	83.9	86.6	79.1	87.2	86.5

1. Wolfram and Harrison, J. Am. Ceram. Soc. 8, 738 (1925).

4. E. P. Poste, J. Am. Ceram. Soc. 2, 944 (1919).

6. R. R. Danielson, J. Am. Ceram. Soc. 6, 634 (1923).

6. J. B. Shaw, Bur. of Std. Tech. Paper, 165.

7-8. R. R. Danielson, J. Am. Ceram. Soc. 3, 961 (1920).

10. H. G. Wolfram, J. Am. Ceram. Soc. 7, 3 (1924).

11. R. D. Landrum, Trans. Am. Ceram. Soc. 14, 756 (1912).

TABLE 21—(Continued)
SHEET IRON GROUND COAT COMPOSITIONS
BATCH COMPOSITION

	16 64	17 63A	18 63B	19 60A	20 8A	21 15A	22 15B	23 15C	24 15D	Max.	Min.	Ave.	Med.	½	Range
Feldspar	23.6	31.0	29.2	26.6	32.4	30.0	30.2	33.8	35.5	38.8	20.5	30.3	30.9	29.65	18.3
Borax	30.9	28.5	29.2	34.9	23.0	22.2	28.1	33.7	29.2	43.8	22.2	31.6	30.4	33.0	21.6
Quartz	20.0	18.9	21.0	21.4	23.8	28.1	20.1	16.9	22.7	29.0	11.2	20.0	20.0	20.0	17.8
Soda ash	6.4	6.0	8.6	7.4	14.0	6.4	10.6	2.4	5.3	14.2	0.0	6.7	6.4	7.1	14.3
Soda nitrate	4.5	4.7	4.8	4.0	4.3	3.9	3.8	3.8	5.2	11.4	0.0	3.8	4.2	5.7	11.4
Fluorspar	5.4	6.7	3.8	3.5		5.0	6.0	3.1		7.5	0.0	4.6	4.8	3.8	7.5
Cryolite			2.0							2.0	0.0	0.1	0.0	1.0	2.0
Red lead										8.3	0.0	0.3	0.0	4.2	8.3
Whiting				2.2						2.2	0.0	0.2	0.0	1.1	2.2
Barium carbonate										2.0	0.0	0.1	0.0	1.0	2.0
Clay	2.3	0.7	0.4							3.9	0.0	0.1	0.0	0.0	3.9
Cobalt oxide	5.4	3.5	0.6		0.5	0.4	0.2	0.3	0.6	2.3	0.0	0.5	0.4	1.2	2.3
Manganese dioxide	1.5		0.4		2.0	4.0	1.0	1.0	1.6	5.4	0.0	1.5	1.0	2.7	5.4
Nickel oxide										1.5	0.0	0.2	0.0	0.8	1.5
Copper oxide										0.6	0.0		0.0	0.0	0.6
Feldspar + Borax + Quartz	74.5	78.4	79.4	82.9	79.2	80.3	78.4	89.4	87.4	91.8	75.2	81.8	80.0	83.1	17.3

MELTED COMPOSITION

	18.6	21.6	20.8	23.7	10.3	21.2	18.5	19.4	23.7	16.4	19.7	19.4	20.0	7.3
Potassium and Sodium oxide	18.0	13.4	16.6	10.3	9.6	13.3	15.2	13.3	20.6	10.3	14.6	14.0	15.4	10.3
Boric oxide	14.1	12.7	6.4	7.3	6.5	6.9	8.8	8.0	9.2	5.0	7.2	7.2	7.1	4.2
Alumina	5.4	7.1		55.6	56.4	49.6	52.1	56.6	56.6	44.1	50.5	49.7	52.2	12.5
Silica	44.1	48.1	50.1	5.5	5.9	7.5	3.8		9.1	0.0	5.1	5.9	4.6	9.1
Calcium fluoride	6.8	8.2	4.5						2.0	0.0	0.08	0.0	1.0	2.0
Calcium oxide			1.6						2.0	0.0	0.0	0.0	1.0	2.0
Cobalt oxide	2.9	0.9		0.6	0.5	0.2	0.4	0.7	2.9	0.0	0.6	0.5	1.4	2.9
Manganese oxide	6.8	4.3		2.5	4.8	1.3	1.2	2.0	6.8	0.0	1.9	1.2	3.4	6.8
Nickel oxide	1.9								1.9	0.0	0.2	0.0	0.9	1.9
Copper oxide									0.7	0.0	0.0	0.0	0.3	0.7
Fluorine									1.2	0.0		0.0	0.6	1.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0					
Alkali + Boric oxide + Silic.	76.2	79.4	87.3	89.6	82.3	83.1	87.2	87.4						

16. J. Bardush, Cer. Ind. 6, 482 (1926).
17-18. F. M. Burt, Cer. Ind. 8, 216 (1927).

19. Danielson and Menzel, Int. Crit. Tab., II, 114.
20. B. A. Sweeley, J. Am. Ceram. Soc. 5, 265 (1922).

on each other. In this diagram, the shaded portion covers most of the area. The white area contains the only compositions showing promise of giving good enamels.

Since the area of good compositions is very small, the possible limits of compositions of good ground coats must be comparatively narrow.

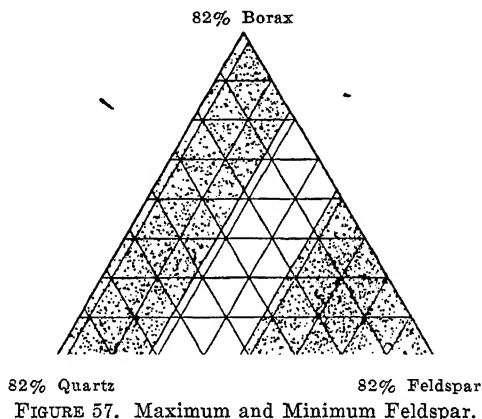


FIGURE 57. Maximum and Minimum Feldspar.

It is highly probable that the great majority of the ground coats whose compositions are secretly guarded could be well fitted into this diagram.

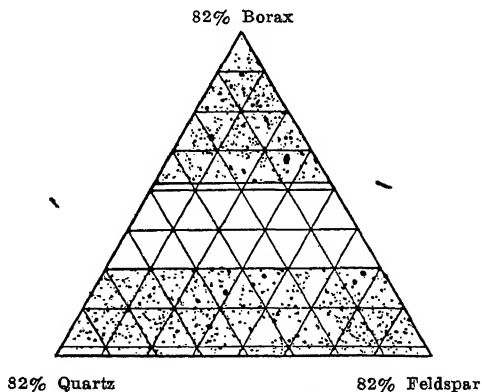


FIGURE 58. Maximum and Minimum Borax.

The author has studied this field of composition very carefully and has varied the total feldspar, borax, and quartz from 78 to 86 per cent. The enamels high in these constituents are more refractory, while those low are very fusible. It is doubtful if good commercial ground coats could be made outside of these limits, but it is possible, where two-frit

enamels are being made, to combine certain compositions which are outside, but close to the area. The resulting composition should, however, fall within the area. Where two-frit ground coats are made, one is usually much more fusible than the other. By blending these two frits, the hardness of the resulting ground coat can be controlled. Two-frit ground coats are convenient where the same frits are desired for many different conditions. They usually have a somewhat longer firing range than one-frit ground coats, which tends to eliminate defects.

The enamels high in feldspar are refractory and have a viscous character, as indicated by a wavy surface after firing. They have

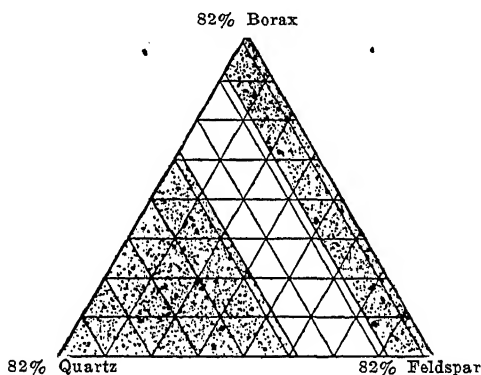


FIGURE 59. Maximum and Minimum Quartz.

good mechanical strength, a good gloss, a good resistance to solution, and their working properties are fairly good.

The enamels with a high quartz content are difficult to smelt and fire because of their refractoriness. They do not fire down to a clear glass, since they contain an excessive amount of bubbles. They have a long firing range, good mechanical strength, a slightly inferior adherence, and a tendency to form large fishscale.

The batch compositions of the enamels are indicated by the points in the diagram, Figure 60. Composition number four is a very good ground coat with good working properties. It is in the center of the field surrounded by compositions number one, two, three, five, six, and seven, which are also good ground coats. It is evident, therefore, from the chart that composition number four could vary more than five per cent in feldspar, borax, or quartz and still be a good enamel.

If this much variation were encountered, however, it would seriously affect the necessary firing conditions of the enamel. Condi-

tions suitable for enamel number six, for instance, would be much too severe for enamel number two. Compositions higher in borax can be used, but they have a short firing range and they tend to fishscale if overfired. Compositions higher in quartz and feldspar are quite refractory, but they can be used, if carefully handled.

The total sodium oxide added by the soda ash and soda nitre must not be excessive since this leads to a pimply surface, poor mechanical strength and too high a coefficient of expansion. Too low an amount tends toward refractoriness and the formation of fishscale. The soda nitre is the first constituent in the raw batch to melt during the smelting; therefore it serves to start the chemical action in that opera-

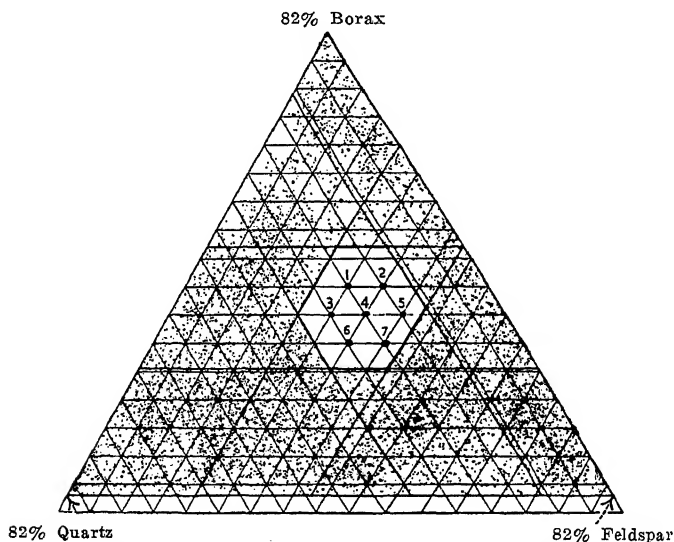


FIGURE 60. Figures 57, 58, and 59 Superimposed.

tion. It is an oxidizing agent, but being more expensive than soda ash, it is not usually added in excess of four per cent, which is sufficient in almost any ground coat enamel.

The fluorspar in a cobalt ground coat makes the enamel more mobile and easy to work. If it is added in excess, the fluorine tends to form a pimply surface, and the enamel is very soluble in acid solutions. If too little or no fluorspar is used, the enamel is difficult to work and has a tendency to copper-head. Cryolite can be substituted for fluorspar, but it is more expensive and is not often used.

An excess of cobalt oxide or manganese dioxide is rare as these constituents are used sparingly because of their cost. Cobalt oxide in

quantities up to five per cent does not appreciably affect the enamel except in intensifying the blue color. In some enamels the cobalt oxide can be reduced to 0.2 per cent and the enamel will still retain its adherence to the iron. If too little is added, the adherence becomes weak and chipping is common. It is generally considered that the adherence of the enamel is aided by manganese dioxide in the presence of cobalt oxide, but alone it is a very poor substitute. It acts as a flux in the enamel, but, if added in large amounts it tends to form a dull scum-like or mat surface. Sometimes nickel oxide, copper oxide, and iron oxide are also added in small amounts (0.1 to 1.5 per cent), but with the exception of nickel oxide they have little, if any, effect on the adherence. They all act as fluxes and affect the color of the ground coat, either by darkening the blue or forming a brown or black color.

Such materials as titanium oxide and zirconium oxide have been added to cobalt ground coats, but the advantage of these materials is questionable. Titanium oxide, as rutile, can be safely added in amounts up to seven or eight per cent, but in excess it forms crystals of sodium titanate and calcium titanate, which give the enamel a matt surface tending towards a gray color. In smaller amounts, the enamel becomes brown. If the titanium oxide replaces silica, it lowers the fusion temperature, but it also shortens the firing range and has a tendency to burn off at the edges and to fishscale.

The use of zirconium oxide has been reported to increase the mechanical resistance of the enamel. It makes the enamel more refractory, even when replacing silica, and is almost never used in commercial ground coats.

In rare cases such materials as sodium silicate, sodium silicofluoride, sodium fluoride, aluminum fluoride, and zirconium silicate have been tried as cobalt ground coat constituents, but their advantages are not pronounced enough to be definite.

The mill additions, for cobalt ground coats, consist essentially of from four to eight per cent clay and one hundred per cent of frit with the necessary amount of water. Sometimes small amounts of quartz, feldspar, or magnesia are added, a practice which has become more common in America during the past few years. Electrolytes such as borax, soda ash, magnesium carbonate, and other salts are usually added to set up the slip. A complete discussion of mill additions is given in Chapter 9.

WHITE GROUND COATS FOR SHEET IRON

White ground coats, if satisfactory, afford a considerable saving in some types of ware as they eliminate one firing operation. The cobalt

blue ground coats must be covered by two coats of white cover enamel to develop a good finish, while one cover coat over a white ground coat gives first quality ware. In enameling colored ware such as signs or ware with black edging, the importance of the white ground is not very great, but where pure white enamels are being made it offers considerable possibility for savings. The use of the white ground coat, however, has not been very popular, for it is not ordinarily considered to be as dependable as the cobalt ground coat. The single cover, over a white ground, is not usually of quite as good quality as the two cover coats over the blue ground. If there is any reboiling, copper heading, or blistering in the white ground coat, it is likely to show through the single cover coat, thus preventing the ware from passing as first grade. With two cover enamels over a cobalt blue enamel, the chances of covering defects caused by the ground coat are improved. If two covers are put on the defective white ground coated ware only, there is a distinct difference in the appearance, which is objectionable, since the production ware should all look alike. The use of two cover coats over a white ground coat produces nice ware, but this practice is not common because of the added cost.

In general, it is considered that white ground coats offer more difficulty than the blue ground coats, although, as more information is obtained and the technique of using white ground coats is improved, they may become more popular with the enameler. At the present time, experience has shown that the cleaning and pickling of the iron, the iron itself, and the application must be better for a white ground coat than for a blue ground coat.

In preparing the iron surface for white ground coats, it has been shown that the adherence is greatly improved by giving the iron a nickel flash. It is not uncommon to use this flash of nickel even when cobalt ground coats are used as it is believed to reduce fishscale and copper-heading. The nickel flash consists of a simple operation following the pickling of the iron, the rinsed sheets being immersed in a solution containing nickel sulphate or double salts (nickel ammonium sulphate). They are left in this solution about five minutes and are then withdrawn and rinsed. The nickel flash (nickel dip) is fully described in Chapter 5.

The compositions of the white ground coats used with the nickel salts do not differ radically from the typical cobalt ground coats, except that they do not contain color oxides and they do contain opacifiers. The nickel flash furnishes the necessary bond between the enamel and

the iron, it being at least partially dissolved by the enamel, as indicated by the penetration of the color into the iron side of the enamel coating. The use of tin oxide and titanium oxide must be avoided in any white ground coat, but the use of zirconium oxide and antimony oxide as opacifiers serves very well.

TABLE 22
WHITE GROUND COATS FOR SHEET IRON

	1	2	3	4	5	6	7	8	9	10
Feldspar.....	15.0	23.5	27.1	18.8	17.9	22.3	24.3	22.8	20.9
Borax.....	24.4	30.6	27.4	42.7	24.8	38.2	33.7	31.1	17.2	40.2
Quartz.....	16.6	21.2	17.5	20.9	19.8	19.6	22.2	30.0	51.3	22.9
Soda ash.....	8.6	10.6	3.3	4.0	3.7	4.9	5.2	22.4	5.1
Soda nitre.....	6.6	3.5	5.8	6.7	2.5	3.5	7.2	4.7	5.5	4.8
Potash nitre.....	4.4
Fluorspar.....	2.9	3.5	1.6	5.3	5.0	4.9	4.2	6.2	6.1
Cryolite.....	6.6	7.1	3.7	11.0
Kaolin.....	3.7	4.0
Zinc oxide.....	2.7
Red lead.....	3.6
Bone ash.....	4.7
Antimony oxide.....	4.8	1.4
Sodium antimonate.....	5.8
Zirconium oxide.....	3.7	6.2
Sodium silicate.....	7.8
Arsenic oxide.....	1.6
Cullet.....	0.3
Barium carbonate.....	4.9
Cobalt oxide.....	0.5
Manganese dioxide.....	1.4

MILL ADDITIONS

	1	2	3	4	5	6	7	8	9	10
Frit.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Clay.....	4.0	5.0	7.0	4.0	5.0	5.0	5.0	5.0
Zirconium oxide.....	6.0	4.0	3.0	8.0	6.0	6.0	6.0	6.0
Nickel sulphate.....	0.1
Magnesium oxide.....	0.5
Ammonium carbonate.....	0.2	0.2
Calcined clay.....	10.0
Magnesium carbonate.....	0.5	0.5	0.5	0.5	0.5
Quartz.....	4.5
Cadmium sulphide.....	1.7

White ground coats used without the nickel flash are not generally as successful as those using it. They must not contain any easily reducible oxides, but they usually contain antimony compounds or arsenic oxide, which seem to contribute considerably to the adherence. The latter oxide is too dangerous to use, because of its poisonous nature, but the former is quite satisfactory. The enamel frit batch and the mill additions may contain zirconium oxide, which is the most

suitable opacifier for white ground coats. It is not reduced by contact with the iron; therefore it retains its white appearance in such enamels.

Typical compositions for white ground coats of both types are shown in Table 22. The enamels using the nickel flash have been used in plant production, but those not using the nickel flash have only been successfully used in laboratory work. These enamels require great care if they are to be satisfactorily employed. Enamels number one and four may be used without the nickel flash, but are better when used with it. Enamels number two, three, five, and six require a nickel flash. It is quite probable that an improvement in the electro-deposition of nickel or some other metals, such as chromium and cobalt, may greatly improve the white ground coat situation.

LIGHT COLORED GROUND COATS

Since white ground coats, because of many defects, have not been popular in the industry, attempts have been made to make them in light colors by introducing only very small amounts (.05 to .2 per cent) of cobalt oxide in the white ground coat. Such a procedure improves the adherence, and such enamels are easier to cover than the blue ground coats. It is quite probable that enamels of this type may come into more common use. Another feature in the employment of white ground coats is the use of colors such as the pastel tints; pink, light blue, and yellow, which are obtained by adding color oxides or stains to the mill additions of white and light colored ground coats.

WHITE COVER ENAMELS FOR SHEET IRON

White sheet iron cover enamels must be pleasing to the eye with a soft white glossy finish and good covering power. Such enamels should fuse at a temperature not greater than that of the ground coat. They should be resistant to solution in materials with which they come in contact and should not be easily stained or discolored. Many cover enamels are exposed to acid fruit and vegetable juices, alkaline cleaners, weather conditions, and even chemical corrosion. If these enamels are used for food containers, their solution should be very slight at most, and if they contain lead and antimony compounds it is even more necessary that they should be insoluble. The resistance of cover enamels to abrasion is great, but the mechanical shock which they will withstand is limited. They are not particularly sensitive to sudden temperature changes, but severe heating and cooling will develop cracks in most cover enamels.

White cover enamels for sheet iron carry opacifiers in both the frit and in the mill addition. The common frit opacifiers are the fluorides

and the antimony compounds. The opacifiers added at the mill are generally tin oxide and zirconium oxide. The mill additions for cover enamels generally include five to seven per cent of a light burning clay, but in some cases a gum is used. Electrolytes may or may not be used, depending on the conditions as outlined in Chapter 5.

The batch composition of the frit seldom contains any form of lead, although acid-resisting enamels may contain as high as ten per cent of lead oxide, which is, of course, not dangerous, if the enamel is insoluble.

Taking 24 white sheet iron cover enamel compositions, as shown in Table 23, and averaging the different constituents, it can be seen that the predominating constituents are: feldspar, borax, quartz, soda ash, soda nitre, fluorspar, and cryolite. If the amounts of feldspar plus borax plus quartz are taken, as shown at the bottom of each column, it will be noted that they vary from 64 to 81 per cent. They average 72.5 per cent and in few cases vary from the limits of 69 to 75 per cent. By plotting the maximum and minimum for feldspar, borax, and quartz on a triaxial diagram as shown in Figure 61, it is evident that a definite area is outlined. The compositions within this area give the best results for sheet iron cover enamels. The points on the diagram in Figure 62 indicate compositions made in checking this reasoning. As in the diagram for cobalt ground coat compositions, the characteristics of the enamels vary with their position on the diagram. With a high borax content the enamels become more fusible, their gloss is good, they are rather soluble, and they are easily overfired. High feldspar content gives a viscous enamel with a tendency toward a wavy surface and refractoriness. The enamels high in quartz are very refractory and difficult to fire to a good gloss. They are very resistant to solution by acids, but the quality of the appearance is not as high as those near the center of the area.

Referring again to the table of 24 sheet iron cover enamels and the summary at the right of the table, it can be noted that the constituents other than feldspar, borax and quartz are chiefly limited to soda ash, sodium nitrate, fluorspar, and cryolite with small amounts of antimony compounds, zinc oxide, whiting, barium carbonate, magnesium carbonate, and clay.

The soda ash and soda nitre together generally amount to about ten per cent of the composition of the enamel. They contribute sodium oxide to the enamel, which increases its fusibility, and its thermal coefficient of expansion. If added in excess, the enamel crazes and has a tendency to form an eggshell surface. The soda nitre functions in the enamel as an oxidizing agent and flux, as it has the lowest melting

TABLE 23. SHEET IRON WHITE COVER ENAMEL COMPOSITIONS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pat.....	25.0	22.0	50.5	32.0	25.0	31.0	31.0	23.7	49.5	48.8	38.6	38.3	22.7	19.3	19.3
z.....	25.5	20.0	30.4	25.0	28.0	27.0	21.0	16.9	27.4	20.4	15.4	39.6	23.9	27.6	22.3
ta.....	21.0	22.0	18.0	19.0	19.0	17.0	22.0	28.2	5.0	11.6	19.0	2.6	11.0	21.7	27.8
ash.....	3.0	10.8	4.0	4.0	3.5	3.5	3.5	14.4	5.0	4.7	6.5	1.8	5.7	4.1	5.8
nitre.....	3.5	4.5	4.6	3.0	3.5	3.5	3.5	3.1	4.5	4.7	6.5	1.8	5.7	2.7	6.9
spat.....	2.5	2.5	4.4	4.0	5.0	5.0	5.0	5.0	4.1	4.3	1.3	0.1	10.1	9.5	15.6
ite.....	14.0	5.0	10.1	12.0	12.0	12.0	17.0	6.2	9.5	10.2	11.7	12.7	4.5	4.8	1.7
oxide.....	5.0										6.5				
ing.....											1.0	0.1	4.5	4.1	
um carbonate.....		4.0						2.5				3.2			
ssum carbonate.....		4.0		2.0	4.0	1.0	2.0								
ropy oxide.....															
xide.....															
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
lk.....	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
w.....	7	7	7	6	6	6	6	6	7	7	7	7	5	5	5
a oxide.....	8	6		7	7	7	7	7			12				
pat + Borax + Quartz.....	71.5	64.0	80.9	75.0	72.0	75.0	74.0	68.8	76.9	69.2	79.0	77.9	64.2	68.6	70.0

	16	17	18	19	20	21	22	23	24	Max.	Min.	Ave.	Med.	%	Range
pat.....	39.0	38.4	17.7	45.7	38.6	22.0	23.7	38.0	32.0	50.5	17.7	32.2	31.5	34.1	32.8
z.....	15.0	27.8	20.5	32.0	15.4	30.0	16.3	18.0	26.0	39.6	15.0	23.8	24.4	27.3	24.6
ta.....	19.0	1.3	35.3	19.0	19.0	17.5	31.7	22.0	8.0	35.3	0.0	16.1	19.0	17.6	35.3
ash.....	6.0	11.3	1.8	11.4	6.5	13.5	9.4	6.9	9.0	14.4	0.0	5.8	4.05	7.2	14.4
nitre.....	1.0	2.0	1.8	1.7	2.0	2.0	3.1	2.2	3.0	6.9	0.0	3.7	3.5	3.4	6.9
spat.....	1.0	5.3	1.8	1.7	1.3	2.2	3.1	2.2	6.0	10.1	0.0	3.1	3.3	5.0	10.1
ite.....	12.0		19.4		11.7		15.8	12.9	5.0	19.4	0.0	9.9	11.7	9.7	19.4
oxide.....									5.0	5.0	0.0	0.7	0.0	2.5	5.0
ing.....	7.0				6.5				7.0	7.0	0.0	0.8	0.0	3.5	7.0
um carbonate.....					1.0				4.0	4.0	0.0	0.2	0.0	2.0	4.0
nessum carbonate.....	1.0		3.5						3.5	3.5	0.0	0.3	0.0	1.8	3.5
mony oxide.....									1.6	1.6	0.0	0.1	0.0	0.8	1.6
xide.....		13.9		9.2		15.0			4.5	4.5	0.0	0.2	0.0	2.2	4.5
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	11.0	15.0	0.0	0.6	0.0	7.5	15.0
lk.....															
ay.....					84		90	85	86						
n oxide.....					6		4	5	6						
pat + Borax + Quartz.....	73.0	67.5	73.5	77.7	73.0	69.5	71.7	78.0	66.0	80.9	64.0	72.1	72.0	71.4	14.9

1. H. G. Wolfram, J. Am. Ceram. Soc., 7, (1924).

2. E. Shaw, Bur. of Std. Tech. Paper, 135, (1923).

3. R. B. Dainton, J. Ceram. Soc., 5, 69, (1923).

4. R. B. Dainton, J. Ceram. Soc., 5, 69, (1923).

5. R. B. Dainton, J. Ceram. Soc., 5, 69, (1923).

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9. R. F. Foste, J. Am. Ceram. Soc., 14, 408 (1931).

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11. R. F. Foste, J. Am. Ceram. Soc., 14, 408 (1931).

12. R. F. Foste, J. Am. Ceram. Soc., 14, 408 (1931).

13. J. Hardman, Cer. Ind., 6, 432 (1926).

14. F. M. Burt, Cer. Ind., 8, 216 (1927).

15. R. A. Swedley, J. Am. Ceram. Soc., 6, 264 (1922).

16. R. A. Swedley, J. Am. Ceram. Soc., 6, 264 (1922).

temperature of any constituent in the batch. As an oxidizing agent, it is very important if antimony compounds are present, since the opacity from antimony compounds depends upon the formation of the higher oxide Sb_2O_5 in the enamel. Four per cent of sodium nitrate is usually all that is necessary and it is included in practically all cover enamels. The soda ash also acts as a flux, but in addition it decomposes during the smelting operation, giving off over forty per cent of its weight as carbon dioxide gas, which not only makes the mass more fusible in the

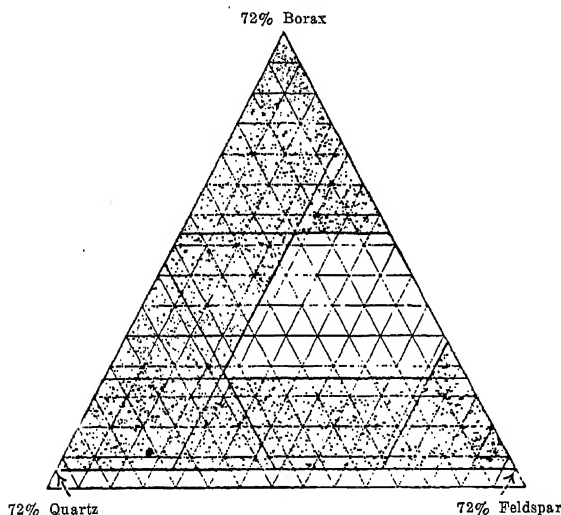


FIGURE 61. Limits for Sheet Iron Cover Enamel Compositions.

early part of melting, but also agitates the batch as it escapes. The amount of soda ash used is influenced by the other materials contributing sodium oxide to the enamel, but it ordinarily varies from four to eight per cent of the batch.

Cryolite and fluorspar in sheet iron cover enamels serve as fluxes and as auxiliary opacifiers. Fluorspar seldom exceeds five per cent of the batch because it does not contribute a pure white, if added in excess, and it has a tendency to give a slightly pimply appearance. It is, moreover, an active flux and it aids opacity considerably. Cryolite is also a good flux and is generally used in cover enamels, sometimes replacing the fluorspar entirely. It is usually added in amounts of from five to twelve per cent, depending upon the presence of other fluxes and antimony compounds. If antimony is present, the opacity

contributed by the cryolite becomes much less important. A field of investigation into the effect of cryolite, fluorspar, and antimony oxide is shown in Figure 63. Here it is evident that a combination of materials rather than the use of one or two alone is desirable to develop good opacity and good quality.

Small amounts of zinc oxide, whiting, magnesium carbonate, and barium carbonate are sometimes used in sheet iron cover enamels. They are particularly useful in enamels low in fluorides, such as acid-

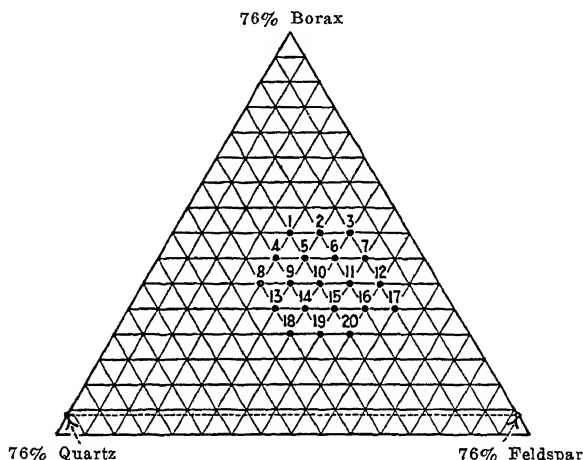


FIGURE 62. Sheet Iron Cover Enamels.

resisting cover enamels. If added in excess, they make the enamel dull in appearance and take the rôle of a refractory rather than a flux. In some enamels zinc oxide seems to aid the opacity somewhat; whiting improves the color, when the discoloration is caused by iron compounds, and barium gives greater mechanical strength and added brilliance. Neither magnesium carbonate nor clay are added to the frit batch in appreciable amounts, since they are not readily absorbed in smelting.

ACID-RESISTING SHEET IRON ENAMELS

. The acid resistance of enamels varies from those stained by fruit juices and water to those which withstand strong acids at elevated temperatures. The acid-resisting enamels are, in general, more difficult to work than the soft enamels. They are less fusible, less fluid, and do not smooth down as easily, which results in more difficulty in making first grade ware. To obtain good acid resistance, some of the ease of making an enamel must be sacrificed.-

The composition of an acid-resisting enamel differs from an ordinary enamel in that the silica content is greater, the fluorine compounds (fluorspar, cryolite, and sodium silicofluoride) are present in smaller amounts, the boric oxide content is reduced, and the remaining constituents are balanced to give the desired fusibility, coefficient of expansion, and the general working properties of the enamel. Too high a boric oxide content will result in an enamel which tears easily, necessitating much greater care in application. It is often desirable to introduce six or eight per cent of lead oxide to avoid this tendency to tear and also to improve the fusibility of the enamel. The fluorides,

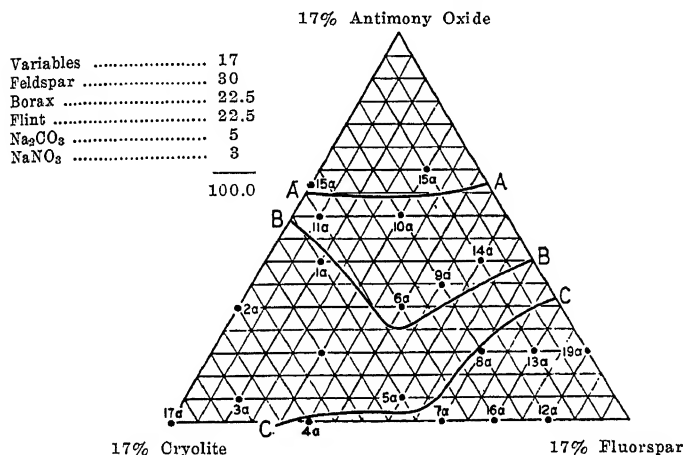


FIGURE 63. Variations of Antimony Oxide, Cryolite, and Fluorspar in Sheet Iron Cover Enamels. Above line A-A, enamels are a refractory glass, and of low opacity; above line B-B, enamels have fair acid resistance; below line C-C, enamels are slightly dull and weak in opacity; between lines A-A and C-C is area of best enamels.

being violent fluxes, aid the fusibility greatly and two or three per cent is generally necessary, not only for this reason, but also to improve the opacity of the enamel. It is not difficult to make an acid-resisting glass of good working properties, but it is very difficult to get good opacity in many of these glasses. The opacifiers do not reduce the acid resistance of enamels, but often improve it. They make the enamel more refractory and give good opacity only with certain glasses. The alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) seldom exceed eighteen per cent of the melted weight as higher percentages tend to cause pinholing and a dull surface. Titanium oxide is used up to eight per cent in many acid-resisting enamels as it contributes about the same acid resistance as silica, but it gives a more mobile enamel. Titanium oxide has the

disadvantage, however, of contributing a yellow or cream color to the enamel. This can be eliminated or reduced by adding one or two per cent of sodium silicofluoride to the raw batch before smelting. The exact nature of the reaction is not understood, but it gives satisfactory results in many cases. It has been found that a substitution of sodium silicate for an equivalent amount of soda ash and quartz in the batch of some enamels greatly improves their acid resistance. This is probably true because enamels made from sodium silicate are more uniform after smelting than those in which the equivalent amount of soda ash and quartz are used. [In smelting enamels, the fluxes (soda nitre, borax, and soda ash) melt first and then progressively take the other constituents into solution in them. If this dissolving action is incomplete, the enamel is not uniform throughout and the properties of the enamel are not the same as they would have been had the solution been complete. In using sodium silicate, part of the silica is already dissolved in the fusible sodium silicate glass, therefore less remains for solution during the smelting. An acid-resisting enamel requires a balance of the constituents present (basic, neutral, and acid) and, therefore, incomplete smelting is detrimental since it upsets this balance. If an enamel is properly smelted, the acid resistance is not affected by this operation.]

The fineness of grinding, the methods of application, and the drying are unimportant from the standpoint of the acid resistance of the enamel.

• The firing time and temperature often influence the acid resistance of an enamel to a great extent. The variation in the temperature in different parts of the furnace may be sufficient to decide whether an enamel is acid resisting or not. The higher the temperature and the longer the firing time, the greater the acid resistance in most cases. In some enamels, the acid resistance is not affected by the firing time and temperature, the property being unchanged regardless of these conditions. The acid resistance of dry process cast iron enamels is not influenced to any great extent by the firing time and temperature, but the acid resistance of sheet iron enamels may or may not be affected.

Greater care is necessary in producing acid-resisting enamels, but where this property is desirable, it can be attained.

Referring to the feldspar-borax-quartz diagram for sheet iron cover enamels, those higher in quartz in the good area are the most promising for acid resistance. Other changes in the composition are, however, necessary. The cryolite and fluorspar are very detrimental to acid resistance and, therefore, must be reduced to a minimum which

is usually not over three per cent. This reduction from seventeen to three per cent means that other constituents must be added to make up the difference. If lead is not objectionable, it may be added up to nine per cent. Barium carbonate, zinc oxide, and sodium antimonate will readily account for the remaining five per cent. If an acid-resisting enamel is being made, it is preferable to add the antimony as the sodium antimonate; as in this manner the maximum opacity is obtained with the least increase in refractoriness. In acid-resisting cover enamels the deficiency of cryolite is sometimes made up by increasing the feldspar, borax, and quartz as a group, to a total of 83 per cent or even more. This gives an enamel relatively high in boric oxide. If the boric oxide is increased too much, however, it causes the enamel to tear during the early stages of firing.

Since clay, added as a mill addition, decreases the acid resistance and acts as a refractory, it is kept at a minimum, which is usually less than five per cent. The other mill additions are similar to those of other sheet iron cover enamels, using such opacifiers as zirconium and tin oxides.

COLORED ENAMELS FOR SHEET IRON

Colored sheet iron cover enamels are, in general, based on a glassy frit. This frit may be a clear glass or may contain some opacity to give it body. The colors are added at the mill, although for blues and blacks the color material may be in the frit. It is obvious that frits of many colors would be impractical because of contamination in smelting, unless a different smelter were used for each color, a condition which would not be economical. The color materials added to the mill batch are, in general, purchased from the chemical supply houses and are not made in the enameling plants. These color materials are usually, color oxides mixed with clay, quartz, and fluxes, and then calcined and ground. A pure color oxide is not readily diffused through an enamel when added at the mill, therefore the prepared color oxides or colored stains are more commonly used.

In the discussion of mill additions and colors more detail is given concerning the making of colored enamels.

The glaze composition used as the basis for colored enamels is not unlike the sheet iron ground coat composition with the cobalt and manganese left out. It does, however, contain four or five per cent of cryolite and slightly less fluorspar and soda ash. Several typical compositions are shown in Table 24. The feldspar, borax, and quartz constitute about four-fifths of the composition, the rest being five to

ten per cent of soda ash, three to eight per cent of soda nitre, three to seven per cent of fluorspar, and five to six per cent of cryolite.*

The mill addition consists of five to seven per cent of clay with the pre-determined amounts of color oxides and opacifiers.

Blue sign enamels are also similar in composition to the ground coats, but they contain about five per cent of cobalt oxide, or cobalt oxide together with a much smaller amount of iron, manganese, or

TABLE 24
SPECIAL SHEET IRON COVER ENAMEL COMPOSITIONS

<i>Material</i>	<i>Sign Blue</i>	<i>Dark Blue</i>	<i>Color</i>	<i>Glaze</i>	<i>Colored Glass</i>	<i>Black</i>	<i>Black Edging Enamel¹¹</i>
Feldspar.....	26.0	15.0	24.0	14.0	11.5	30.0	18.9
Borax.....	28.0	26.0	29.0	29.0	24.0	28.0	36.3
Quartz.....	22.0	26.0	30.0	28.0	16.8	20.0	15.7
Soda ash.....	7.0	7.0	10.0	10.0	13.2	3.0	8.7
Soda nitre.....	4.0	3.0	3.0	5.0	5.0	3.0	4.4
Fluorspar.....	5.0	4.0	7.0	2.9	5.0	7.0
Cryolite.....	4.0	4.0	7.0	2.2
Red lead.....	4.5	11.3	4.4
Whiting.....	5.2	1.5
Zinc oxide.....	6.0	3.09
Barium carbonate.....	1.9
Manganese dioxide.....	3.0	4.0
Cobalt oxide.....	4.0	7.0	3.0	2.0
Ferrie oxide.....	1.5	2.2
Rutile.....
Copper oxide.....	2.0
Iron oxide (black).....	1.0
Chromic oxide.....	2.0

nickel oxides to darken the blue color. A small amount of rutile in the enamel helps to darken the cobalt blue color and reduces the amount of cobalt necessary. The fluorine compounds are, in general, kept low since blue sign enamel must resist weather to avoid deterioration of the surface called "fading." The fading of a blue sign enamel is not actually a fading at all; it is the result of an etching of the surface of the enamel, giving the appearance of ground glass. On removal of this rough surface by either grinding or re-firing, the original cobalt blue

* The presence of lead oxide must be considered, however, for it often has a decided effect on the color produced by any given color oxide or stain. In any case the mill addition or combination in the composition requires a cut-and-try method to get the particular color desired. There are no rules for the additions necessary to obtain a given color in different enamel compositions.

¹¹ T. Davies, Cer. Ind., 17, 186 (1931).

color is brought back. The mill addition consists principally of about five per cent of clay or a gum, the latter being commonly preferred since the clay decreases the resistance to weather. The control of the amount of gum is important because of the brushing operation. Too much gum makes the enamel dry so hard that it is difficult to brush it through the stencils, while too low a gum content results in damage to the coating which is then not sufficiently firm. Table 24 shows the compositions of several good sign enamels.

Beading Enamels. Black edging enamel is usually made by milling a black frit very fine, with a mill addition of black oxide. A good black is difficult to obtain as there is usually a tendency toward either a brown black or a blue black. The proper proportioning of the color oxides can only be found for a given enamel by experimentation. The black edging enamel is usually milled finer than the ground coat and, if applied over the unfired ground coat, it is applied as a fairly dry spray. This can be accomplished by using a heavy, finely ground slip, by using high air pressure on the atomizing jet of the gun, or by holding the spray gun at some distance from the ware. The first method is recommended. Although it has become a common practice to fire the ground coat and black edging together, the safest method of obtaining all first grade ware is that of making this a two-fire operation.

GRAY MOTTLED ENAMELS

The gray mottled enamel is of the one-coat type, introducing all the problems incidental to a one-coat enamel. The ware must be completely covered, in one operation, without bare spots or blemishes. This one coat must show two colors uniformly distributed, it must have good gloss and lustre, and it must be highly resistant to solution.

In making a mottled enamel, the conditions must be more closely controlled than with the three-coat type. The ordinary good enameling iron is generally used, but the mottling is aided by impurities distributed uniformly in the surface of the sheet. The set of the enamel, its pH value, the clay, and the salt content must be controlled. Such salts as magnesium, cobalt, and iron sulphates, called mottling salts, are used. The preparation of the steel, the application, and the temperature and humidity of drying must be under careful control.

The compositions of gray mottled enamels have undergone considerable change. The early types were similar to 1, the intermediate types to 2, and the more modern types to 3, 4, 5, 6, and 7, of Table 25.

Color oxides, such as iron, cobalt, manganese, and nickel oxides, are sometimes used to control the shade of the gray.¹ These colors are mixed in the raw batch before smelting, while the sulphates which promote the mottling are added at the mill. The mill additions usually consist of about six per cent clay, an electrolyte such as magnesium sulphate,

TABLE 25
GRAY MOTTLED ENAMEL COMPOSITIONS

	1	2	3	4	5	6	7
Feldspar.....	30.0	40.0	48.0	33.5	48.0	38.0	16.5
Borax.....	28.5	30.5	40.0	24.5	29.0	28.0	12.5
Quartz.....	19.0	10.0	15.0	12.0	6.0
Soda ash.....	8.0	6.5	3.0	12.5	3.0	4.5	4.0
Soda nitre.....	4.0	5.5	4.0	3.8	3.0	4.5	1.6
Fluorspar.....	3.0	1.5	6.7	4.0	5.0	1.5
Bone ash.....	5.0	4.5	3.5	3.8	3.0	0.9
Cryolite.....	3.2	3.5	4.0
Antimony oxide.....	2.5	1.5	1.5	1.5	2.0	2.0	1.0
Black antimony.....	0.7
Sodium sulphate.....	0.6
Cobalt oxide.....	0.1
Manganese dioxide.....	0.3

1-2-3. R. R. Danielson, Jour. Am. Ceram. Soc., 3, 961 (1920).

4-5-6. H. C. Arnold, Jour. Am. Ceram. Soc., 5, 858 (1922).

7. F. M. Burt, Cer. Ind., 8, 216 (1927).

frit, and water. The slip is milled to pass a number eighty sieve and is usually allowed to age three or four days. For further information on the control of the slip, see Chapter 10.

WET PROCESS CAST IRON ENAMELS

Although wet process cast iron enamels are much more troublesome to the enameler than any other type, there is less published information about them than of the others. The difficulties encountered with them may be caused by the fact that our knowledge is so limited. Wet process cast iron enamels are used extensively on stove parts and other light weight cast iron wares. The fusion temperature is generally quite low (1200 to 1400° F) since the light castings will warp and sag if heated at higher temperatures. The time of heating depends upon the weight of the casting and the equipment used, normally requiring about fifteen minutes. These enamels are made in white, black, and all colors, but they are never of as good quality as the other types of enamels. They do not usually show quite as good a gloss and they will not withstand quite as severe mechanical abuse. They are more

soluble, and since most compositions contain lead, they are not suitable for cooking ware. The introduction of leadless wet process cast iron enamels has only been considered successful within the past few years. The old lead-bearing type, however, holds favor in many plants and is as yet the more commonly used wet process cast iron enamel.

These enamels may or may not be used with a ground coat. However, the ground coat need not contain cobalt or other color oxides, as does the sheet iron ground coat. The ground coat is often merely a cover enamel with weak opacity. The use of zirconium oxide as an opacifier has greatly aided the opacifying of this first coat on cast iron. Easily reducible oxides must be eliminated from the ground coat to avoid the formation of blisters while firing the finish coat over the ground.

The compositions of wet process cast iron enamels do not lend themselves to graphic representation as do those for sheet iron enamels. The compositions are more complicated and sensitive to variation. Table 26 shows the frit batch compositions and the melted weight compositions of a series of representative wet process cast iron enamels. These may be divided into three groups; the leadless enamels numbers nine, ten, eleven, and twelve; the low-lead enamels numbers one, two, three, four, five, six, and seven; and the high-lead enamels number eight. The leadless enamels are new and less thoroughly developed than those containing lead. On observation, it will be noted that the leadless enamels approach the compositions of sheet iron cover enamels, from which they were probably derived. The fusibility, however, has been improved by small additions of fluxes such as barium carbonate, and zinc oxide. In number eleven the silica shows a decided reduction and in all of these enamels the borax is raised to the maximum which the enamel will carry. An excess of boric oxide induces crawling or tearing of the enamels, a defect characteristic of some leadless wet process cast iron compositions. Number twelve is a zirconium enamel of a distinctly different type from any of the others. There is still considerable opportunity for study in the leadless type of enamel, and much improvement will probably come with more thorough investigation.

The high-lead wet process cast iron enamels may contain up to 45 per cent of lead oxide, but the tendency is toward a reduction rather than an increase in the lead content. These enamels are easily worked and have brilliant surfaces.

The ordinary low-lead enamel of this type is usually opacified in the frit by antimony compounds. If the lead is high, there is a tendency toward a cream or a yellow color, the latter being particularly

TABLE 26. WET PROCESS CAST IRON ENAMEL COMPOSITIONS

	LOW-LEAD							HIGH-LEAD	LEAD-LESS			
	1	2	3	4	5	6	7		8	9	10	11
Feldspar.....	22.3	12.7	13.2	12.8	13.4	25.0	20.0	17.3	22.4	22.4	21.7	25.96
Borax.....	26.8	23.8	21.7	23.5	22.0	25.0	20.0	18.3	26.9	26.9	31.0	46.50
Quartz.....	18.2	8.8	12.4	12.1	12.6	15.0	10.0	10.6	22.3	22.3	7.0
Soda ash.....	4.3	5.9	6.0	4.3	4.3	2.4	5.56
Soda nitre.....	6.7	2.6	3.0	2.0	4.2	8.0	4.0	4.8	6.7	6.7	5.7	3.50
Fluorapat.....	4.6	3.5	2.7	2.7	2.8	7.0	10.0	8.7	4.6	4.6	7.6	5.00
Oryolite.....	5.5	5.3	8.8	5.1	9.0	2.9	5.5	5.5
Red lead.....	8.9	11.3	14.3	14.8	17.1	15.0	15.0	30.7
Zinc oxide.....	6.1	7.0	6.8	7.1	5.0	5.0	4.8	4.2	7.0	12.00
Barium carbonate.....	12.7	8.8	8.5	8.9	4.2	8.6
Whiting.....	5.3	4.4	4.5
Meltopax.....
Boric acid.....	3.5	2.9	1.9
Opax.....	4.4	5.0	4.5
Antimony oxide.....	3.1	3.1	3.1
Sodium antimonate.....	4.4	4.3	4.5
Feldspar + Borax + Quartz.....	67.3	45.3	47.3	48.4	48.0	65.0	50.0	46.2	71.6	71.6	59.7

MELTED COMPOSITION

	1	2	3	4	5	6	7	8	9	10	11	12
KNaO.....	18.5	10.9	16.0	11.4	13.1	13.3	14.1	9.4	18.8	18.9	16.1	20.10
Na ₂ O.....	14.1	9.0	14.2	9.6	11.3	8.3	10.0	7.1	14.2	14.3	11.2	16.88
K ₂ O.....	4.5	1.9	1.8	1.8	1.8	5.0	4.1	2.3	4.6	4.6	4.9	3.22
B ₂ O ₃	11.8	13.4	9.1	12.2	9.1	10.9	8.9	8.7	11.8	12.0	14.9	17.02
Boric oxide.....	10.4	13.4	16.0	17.1	18.8	17.4	17.8	33.6
Lead oxide.....	6.4	4.6	5.4	4.5	5.4	5.5	4.5	4.6	6.5	6.5	5.3	5.30
Al ₂ O ₃	39.0	2.9	24.0	24.3	24.0	37.0	28.0	24.6	44.2	44.7	27.8	24.80
Silica.....	6.2	5.6	7.0	4.8	7.1	4.0	5.9	6.5	6.2	6.3	4.9	2.40
Fluorine.....	3.9	6.7	2.3	5.2	2.3	5.9	8.7	7.1	4.0	4.0	10.5	3.6
CaO.....	12.0	7.9	7.9	7.8
Barium oxide.....	5.4
MgO.....	7.5	8.0	8.0	8.2	5.9	6.1	5.4	5.0	9.2	12.00
Zinc oxide.....
Antimony oxide.....	3.7	4.2	4.3	4.3	3.7	3.8
Sb ₂ O ₃	4.7	6.1	5.9	15.78
ZrO ₂

2. W. N. Knowles, Cer. Ind., 8, 48 (1927).
3 and 5. R. R. Danielson, J. Am. Ceram. Soc., 12, 543 (1929).
12. Titanium Alloy Manufacturing Company.

objectionable. It is often masked by the use of a complementary color, such as the blue from cobalt oxide, but this is, of course, difficult to control. Uniformity of the white color in these enamels is very important, since parts made at widely different times may be assembled on the same stove and they must match.

On observing the compositions of the low lead wet process cast iron enamels, it will be noticed that the feldspar, borax, and quartz together make up only about half of the composition. Soda ash is low. Soda nitre greatly aids the opacity from antimony compounds since it promotes the formation of the pentoxide by oxidation. The lead oxide varies from nine to seventeen per cent with about fourteen per cent as average. Most of these enamels contain barium carbonate which, to a certain extent, acts as a substitute for lead oxide. Zinc oxide, whiting, and boric oxide are also added as fluxes.

The mill additions of these enamels are similar to those for sheet iron enamels. A fat clay is generally used and from five to seven per cent of the weight of the frit is added. Four to eight per cent of either tin oxide, zirconium oxide, or both, are added to give opacity. Electrolytes are used only for suspension and to control the slip for spraying, as all wet process cast iron enamels are sprayed.

The colored enamels are generally made by omitting the opacifier from the mill addition and adding the appropriate amount of the color oxide or stain desired. With lead-bearing enamels, the choice of stains and color oxides is more restricted than with leadless enamels, because the lead often affects the color to a marked degree. (See discussion of mill additions, page 247.) Such colors as black or dark blue are often made from colored frits. Black is a difficult color to obtain by mill additions alone and is, in general, much more satisfactory if made by including black oxide in the mill addition of a black frit. Since these dark colored frits can be made in the ground coat smelter, additional equipment is not required.

‘ DRY PROCESS CAST IRON ENAMELS

The enamels used in the dry process or powder method of enameling cast iron are more complicated in composition than those used for sheet iron. They contain more constituents in the form of fluxes and, since the opacity must be developed almost entirely in the frit, a much better balanced composition is necessary.

‘Dry process cast iron enamels are used chiefly on heavy castings such as sanitary ware, pedestals, scales, and barber chairs. They are usually more brilliant than either the sheet iron or wet process cast iron

TABLE 27. DRY PROCESS CAST IRON GROUND COAT COMPOSITIONS

	1	2	3	4	5	6	7	8	9	10
Feldspar.....	35.0	56.5	56.0	38.5	21.5	22.6
Borax.....	30.3	33.8	29.4	29.5	20.9	25.3	30.0	30.1	41.9	34.0
Quartz.....	57.3	58.5	60.2	34.8	15.0	11.0	10.3	21.5	37.8
Soda nitre.....	5.7	3.1	2.6	2.6	4.0	3.6	2.2	3.2
Red lead.....	6.7	4.6	7.5	5.3	23.0	27.6	2.5	4.3	10.8	1.9
Cobalt oxide.....	2.6	0.24
Manganese oxide.....	1.5
Zirconium silicate.....	1.7	1.5
Magnesium carbonate.....	0.6	1.1	1.9

MILL ADDITIONS (Frit = 100)

	1	2	3	4	5	6	7	8	9	10
Clay.....	36.0	5.2	4.2	11.0	8.8	4.0	10.5	5.1	3.5	6.0
Feldspar.....	16.4	14.1
Quartz.....	69.0	9.6	8.8	16.2
Cobalt oxide.....	0.3	0.1
Zirconium silicate.....	2.3

MELTED COMPOSITIONS

	1	2	3	4	5	6	7	8	9	10
Potassium sodium oxide, KNaO.....	8.5	11.4	11.5	16.1	13.9	13.5	10.8	10.6
Sodium oxide, Na ₂ O.....	4.3	7.6	6.7	4.3	4.4	5.5	5.2	6.1	7.4	6.3
Potassium oxide, K ₂ O.....	1.8	7.1	7.1	10.6	7.7	7.4	3.4	4.3
Boric oxide, B ₂ O ₃	6.8	14.3	12.1	6.9	7.0	12.3	10.0	13.7	14.3	14.1
Lead oxide, PbO.....	4.0	5.2	7.5	18.4	20.3	2.8	3.8	4.0	9.8	2.2
Alumina Al ₂ O ₃	7.2	2.4	3.8	11.3	10.7	13.2	12.2	10.3	16.6	7.4
Silica, SiO ₂	77.8	70.3	67.8	51.8	50.6	55.1	58.1	58.3	48.0	63.0
Magnesium oxide, MgO.....35	1.0
Cobalt oxide, CoO.....	3.01
Manganese oxide, MnO ₂5
Zirconium silicate, ZrSiO ₄	2.7	1.7

enamels, but the process is generally more expensive.³ It is, however, sometimes used on small castings, the hot casting being pushed into the enamel powder and withdrawn with its coating of enamel which melts down to a smooth layer because of the residual heat in the iron. The method of dusting the enamel onto the hot casting through sieves is much more common as several coatings are usually necessary to produce the best results.

GROUND COATS

Ground coats, often called slush coats or grip coats, are used for all dry process cast iron enameling. These coats serve the purpose of protecting the iron from oxidation and scaling during the heating-up process. They dissolve any iron oxide or impurities on the surface of the casting and also act as an insulating layer to prevent the reduction of any of the constituents of the cover enamel by the iron. They are applied as a thin slip to the clean casting, are allowed to dry and are heated with the casting in preparation for the dusting-on process.

These ground coats must have a long firing range, and must not volatilize or burn off, even when exposed to the enameling temperature for a considerable period of time.⁴

The old type of ground coat for cast iron was merely a sinter, which did not fire down to a good gloss. Examples of these ground coats are shown in Table 27 as one and two, the former being the old German type and the latter the old American type of composition. These compositions, being composed chiefly of quartz and borax, are very refractory and on smelting form a lava-like mass, which never melts down on the iron, but merely remains as a rough sintered layer. The German type contains a large mill addition of both clay and quartz which makes it even more porous than the American type.

The introduction of feldspar into enamel batches followed, and the modern types of enamel were developed. Enamel number three shows the use of two frits, one containing feldspar and approaching the more modern type of ground coat and the other the old sintered type of frit. This type of enamel was used quite extensively. It contains a small amount of cobalt oxide, which is supposed to improve the adherence. The use of cobalt, however, in cast iron ground coats is of questionable value.

The ground coats in Table 27, numbered from four to ten, are typical of modern practice. They are all based on feldspar, borax, and quartz

with additions of fluxes for improving the fusibility. Numbers four and five are of the high lead type with considerable refractory added in the mill additions. Number four is of the one-frit type and number five of the two-frit type of composition. On referring to the chemical compositions, it will be noted that these two ground coats differ from the other modern ones only in the higher lead content and lower boric oxide and silica. They are somewhat more fusible, and the glasses formed are strong mechanically because of the lead content.

The low lead modern ground coats consist of about ninety per cent feldspar, borax, and quartz. They do not, in general, contain large mill additions, the clay being added chiefly for suspending purposes. On considering the chemical composition, the soda and potash total about twelve per cent, the boric oxide about twelve per cent, the alumina about twelve per cent, and the silica about fifty-five per cent. The high silica and alumina give the glass its greater strength while the soda, boric oxide, and lead oxide act as fluxes. The small amounts of magnesia and zirconium silicate are added to improve the firing range, and the cobalt and manganese oxides are added to improve the adherence.

Electrolytes, such as borax, magnesium sulphate, sodium carbonate and sodium silicate are usually added to slips of these ground coats to control the set. The frits are ground very fine and are used in a thin watery condition, which when applied gives a very light coating.

WHITE DRY PROCESS CAST IRON COVER ENAMELS

White dry process cast iron cover enamels vary considerably in composition and properties. The white color may vary from a cream to a blue white. Some of these enamels are so soluble that they are stained by such weak solutions as city waters, and others are so resistant that they will withstand strong acids. Dry process cast iron enamels are, however, very brilliant, durable, and satisfactory in service which makes them very popular.

Compositions of representative types of white cover enamels are shown in Table 28. It will be noted that two each of the following types are given: leadless-tin, low-lead tin, high-lead tin, leadless-antimonate, low-lead antimonate, medium-lead antimonate, and acid resisting. One composition is given for a leadless-antimony oxide, and a medium-lead antimony oxide enamel. This illustrates practically all of the different types of compositions, representative ones being chosen in each case.

Noting these compositions in general, certain characteristics are common to all of them.- In contrast with the enamels previously

studied, quartz additions are conspicuously absent, except in the two acid-resisting compositions. These cover enamels derive practically all of their silica from the feldspar, the amount actually present being about 25 per cent of the melted weight, as shown in the table of chemical compositions, Table 28.

All of these compositions, with the exception of the acid-resisting enamel number fifteen, contain feldspar, borax, zinc oxide, and soda nitre. In very few cases does the feldspar content fall below thirty per cent, most of the compositions containing between 30 and 35 per cent of feldspar. Feldspar is the refractory in this type of enamel contributing all of the silica, most of the alumina and all of the potash. The alumina is essential to good working properties and opacity in most enamels.

The borax content varies considerably from one composition to another with a range (excepting No. 15) of from 13.3 to 34.1 per cent. However, most of the compositions fall between 18 and 26 per cent of borax. The borax is a flux contributing both soda and boric oxide to the glass. In leadless enamels the boric oxide is added at a maximum. Since borax is about one-half water, the actual amount of anhydrous sodium borate which reaches the glass composition is only about nine to thirteen per cent of the raw batch. By referring to the chemical compositions of these enamels, it will be noted that the boric oxide, which is practically always present, amounts to about ten to twelve per cent of the melted weight.

Soda nitre, which is present in all of the compositions in amounts of from 2.4 to 7.4 per cent, is added as an oxidizing agent and as a source of soda. It is the most fusible constituent in the batch and, since it forms a mobile melt, it soaks through the batch during the early melting, even when present in so small an amount, promoting fusion of the other constituents, and oxidation when it reacts with them. Soda nitre does not decompose rapidly below 1500° F unless it is in reaction with other constituents. Soda nitre is particularly important when antimony oxide is used as the opacifier, since the opacity from antimony is due to the formation of the higher oxide which is insoluble in the glass. The compositions in the table show the increased amounts of soda nitre in enamels having antimony oxide present. Sodium nitrate is added to enamels containing lead compounds to prevent the reduction to metallic lead.

Zinc oxide is an important flux in dry process cover enamels. It contributes brilliance and strength to the glass, serving a similar function to lead oxide. It is used to aid the lead, thereby permitting a

TABLE 28. DRY PROCESS CAST IRON COVER ENAMEL COMPOSITIONS

[illegible]

MELTED COMPOSITIONS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Potassium sodium oxide.....	KNaO	12.0	15.1	10.7	14.4	12.7	15.9	20.8	15.5	17.4	17.0	14.9	18.3	15.1	15.8	15.6	18.4	24.6	20.8	20.5	34.8
Sodium oxide.....	Na ₂ O	5.0	11.3	9.9	7.9	6.3	8.5	16.4	8.9	10.8	10.6	8.6	12.3	8.2	8.9	15.6	16.7	17.7	13.1	19.8	24.6
Potassium oxide.....	K ₂ O	7.0	3.8	6.8	6.5	6.4	7.4	4.4	6.6	6.6	6.4	6.3	6.0	6.9	6.9	1.7	5.9	7.7	9.7	10.2
Boric oxide.....	B ₂ O ₃	21.2	18.5	8.2	8.7	7.9	5.7	2.6	12.8	11.0	10.3	10.1	11.1	12.8	8.8	4.9	15.6	17.1	13.0	10.0
Lead oxide.....	PbO	9.2	7.7	16.5	16.6	3.0	5.8	10.0	9.8	8.0	29.8	8.8
Alumina.....	Al ₂ O ₃	7.5	6.2	7.4	7.1	7.0	8.0	6.0	7.2	7.2	6.8	6.9	6.4	7.5	7.5	1.9	6.5	8.3	10.9	11.0
Slime.....	SiO ₂	26.5	25.0	25.9	30.6	24.6	28.3	48.9	25.2	25.2	24.4	24.3	22.9	26.5	26.5	41.6	37.0	47.2	29.4	37.3	39.0
Zinc oxide.....	ZnO	12.5	11.5	10.8	10.3	10.5	5.2	14.0	11.0	9.1	7.0	7.5	14.0	10.0	10.0	5.9	14.3
Barium oxide.....	BaO	7.4	3.9	10.1	6.2	6.2	1.4	7.8	6.2	6.2	10.1
Calcium oxide.....	CaO	1.6	1.7	1.7	1.7	1.7	2.0
Calcium fluoride.....	CaF ₂	8.0	8.5	11.6	5.0	3.2	7.3	7.3	12.0	10.0	10.0	6.0	4.5	9.3	5.2
AlF ₃	AlF ₃	4.8	1.6	1.2	5.0	1.6	1.8	1.7
Aluminum fluoride.....	AlF ₃	7.2	2.4	1.8	7.5	2.4	2.7	2.6
Sodium fluoride.....	NaF
Magnesia.....	MgO
Tin oxide.....	SnO ₂	8.3	8.0	9.4	7.7	9.0	8.6	13	2.8
Antimony oxide.....	Sb ₂ O ₃	8.7	10.0	10.0	13.3	9.2	13.9	6.0	6.4
Bone ash.....	Variable
Titanium oxide.....	TiO ₂	1.9	7.9

reduction in the amount of the latter. The amount added varies from about ten per cent in leadless enamels to about five per cent in high lead enamels.

Soda ash is used in dry process cover enamels to contribute soda when an insufficient amount of the latter is contributed by the borax, soda nitre, cryolite and sodium antimonate.¹ The total soda in the melted compositions of these enamels seldom exceeds eleven per cent, the amount usually being controlled by the coefficient of expansion of the glass. Increases of soda raise the thermal expansion coefficient of the glass very rapidly. If the soda and potash content of the melted weights of the enamel exceed about nineteen per cent, there is a decided tendency for the enamel to be pimply after firing.

Fluorspar is an active flux in these enamels and it greatly aids the development of opacity. It is present in amounts up to eleven per cent in the ordinary compositions for dry process cover enamels; but in acid-resisting enamels, it seldom exceeds two per cent. It reduces the acid resistance, even when added in these smaller amounts. It is usually present, however, since it is very desirable in improving the working properties of the enamel.

Cryolite is not so common a flux as fluorspar but it is a very strong flux. It occurs in many enamels in amounts of about four per cent, but is sometimes present in as much as twelve per cent of the batch weight. It aids the opacity in much the same manner as fluorspar does, the permanent opacifying compound contributed to the enamel by cryolite, being the sodium fluoride. It is questionable if any aluminum fluoride survives the smelting. The alumina contributed aids the alumina from the feldspar in improving the mechanical strength of the glass. Cryolite, like fluorspar, acts to lower the resistance of the enamel to acid solutions. Most of the lead present in enamels is added either as red lead (Pb_3O_4) or litharge (PbO). Since the manufacturers of litharge have made a more fluffy product its use has become general. It is doubtful if the oxygen given off from the Pb_3O_4 in forming PbO aids greatly in enamel making, since this oxygen comes off before the batch has a chance to melt. White lead is not commonly used because of its expense and questionable advantage. The evolution of carbon dioxide and water may aid in stirring the batch, but it is not usually considered worth the additional cost.

Lead oxide (either red lead or litharge) is a very desirable flux in dry process cover enamels. It aids the fusibility and greatly improves the working properties of the enamel. Lead oxide and boric oxide are the only two fluxes which can be added in large amounts to an

enamel glass without promoting devitrification (crystallization). The crystals of the compounds of these oxides form at temperatures below the fusion temperature of the enamel; therefore they have no chance to form in an enamel melt. Devitrification of the glass results in a matt surface enamel not popular for most purposes.

. Lead oxide, because of its poisonous nature, has been avoided as much as possible in enamel manufacture. Dry process cast iron enamels are not ordinarily used on food utensils, therefore there is no danger to the user. In production the necessity of breathing or absorbing soluble lead compounds should be avoided. With good ventilation for the mixing, smelting, and dusting operations, no difficulty from lead poisoning should be encountered. In using lead enamels, however, every precaution should be taken.

Barium carbonate is a valuable flux in small amounts, since it acts similarly to lead oxide. It improves the fusibility, the gloss, and the brilliance. It is seldom added in amounts as high as ten per cent of the batch weight of the enamel.

. Boric acid is used in dry process enamels to contribute boric oxide, when that furnished by the borax is not sufficient. One seldom finds a composition containing both boric acid and soda ash because it is cheaper to add these two constituents as borax. If there is insufficient soda to combine with all the boric oxide, the excess is added as boric acid.

. Sodium silicofluoride is a constituent not common to this type of enamels. It, however, serves a very important function in the acid-resisting compositions containing titanium oxide. The latter tends to produce a yellow colored enamel, but, if one or two per cent of sodium silicofluoride is added to the raw batch, this color disappears. It is a strong flux, but it probably loses its fluorine early in the melting operation, for it decomposes below its melting point. The sodium fluoride may be retained, but the silicon tetrafluoride is probably lost by volatilization.

. Whiting is a source of calcium oxide in an enamel and may be added in small amounts (less than five per cent). It is a refractory and in larger amounts it causes devitrification. It has an important influence on the color of enamels, especially if small quantities of iron are present. The yellow color contributed by the iron is reduced by the addition of whiting to the glass batch. Calcium oxide also has an important effect on the color of antimony enamels. The tendency of these enamels to take on a blue color in melting can often be eliminated by the replacement of lime with other fluxes.

Bone ash is seldom used in enamels, but is considered by some enamellers to improve the adherence and the opacity. The improvement of the opacity is supposed to be particularly important where tin oxide is used as the opacifier.

Two kinds of opacifiers are used in dry process cast iron cover enamels: tin oxide and antimony compounds. The older type of enamels all contain tin oxide, which is the simpler opacifier to use. It is not readily reduced and remains in the enamel glass as SnO_2 , undergoing no chemical change. It is seldom added in amounts exceeding eight per cent of the raw batch.

The antimony opacifiers used are antimony oxide and sodium antimonate. The American antimony oxide is not as pure as the Chinese grade, but it produces a better opacity in enamels.¹³ The antimony oxide tends to make the enamel refractory and is, therefore, seldom added in excess of seven per cent.

Sodium antimonate enamels may contain as much as fifteen per cent of sodium antimonate. The nitrate is not quite so important to the opacity in using the antimonate, and the fusibility of the enamel is not reduced as much as when the antimony oxide is used.

If the lead oxide exceeds nine per cent in antimony oxide enamels, there is a tendency toward a yellow color caused by the formation of lead antimonate. This color may be partially compensated by the addition of small amounts of cobalt oxide, but the control of the color is thus made very difficult.

Clay is seldom added to dry process enamels, since it is not readily absorbed in the batch. If added at all, it is only to the extent of a few per cent acting as a refractory constituent. It is usually considered better to add the alumina and silica as feldspar rather than as clay.

With the development of acid-resisting enamels the use of a pure grade of titanium oxide (not rutile) has become more common. This titanium oxide, although a refractory in the enamel, gives greater fusibility than silica. By replacing up to four per cent of silica by twice as much titanium oxide the fusibility is not changed, but the acid resistance is improved in most enamels. Over eight per cent of titanium oxide causes devitrification in many enamels, which results in poor gloss. The yellow color often resulting in titanium enamels can be compensated by adding one or two per cent of sodium silicofluoride.

The white dry process cast iron cover enamels seldom contain any mill addition, although in rare cases one or two per cent of tin oxide are added at the mill to improve the opacity.

In a consideration of the different types of cover enamels, brief statements will be given to aid in the interpretation of the compositions in Table 28.

Leadless, Tin Enamels. The leadless, tin enamels contain no lead and are opacified by tin oxide. To compensate for the absence of lead oxide, the boric oxide is present in large amounts. Barium oxide, cryolite, fluorspar, and zinc oxide aid the fusibility. No antimony is necessary for the opacity.

Low-lead, Tin Enamels. The addition of six or eight per cent of lead oxide permits a lowering of the boric oxide content. The other fluxes are lowered slightly.

High-lead, Tin Enamels. The addition of fourteen or fifteen per cent of lead oxide results in a decided lowering of the amounts of the other fluxes, such as zinc oxide, boric oxide, and cryolite. The feldspar content does not vary greatly in this series.

Leadless, Antimonate Enamels. These enamel compositions, like the leadless tin enamels, contain considerable amounts of other fluxes, such as boric oxide, zinc oxide, cryolite, and fluorspar. In place of the tin oxide, sodium antimonate is added to these compositions.

Low-lead, Antimonate Enamels. These enamels contain less boric oxide than the leadless type. The zinc oxide and other fluxes are reduced to compensate for the addition of two to five per cent of lead oxide.

Medium-lead, Antimonate Enamels. With a medium-lead content (eight or nine per cent) the other fluxes of the enamel are further reduced. Zinc oxide shows a decided reduction. Higher amounts of lead oxide produce a yellow color in antimony enamels.

The leadless and medium-lead antimony oxide enamels, numbers thirteen and fourteen, are similar to those containing sodium antimonate except for the adjustment for the soda content.

The two acid-resisting enamels differ decidedly in composition. Number fifteen is not a commercial type, but is decidedly acid resistant and can be used where acid resistance is of primary importance. It will withstand boiling hydrochloric acid for hours. It does not flow down to a smooth layer, but is slightly wavy. If applied slowly, a very satisfactory coat can be obtained. Enamel number sixteen is of the commercial production type. It is resistant to fruit acids, but is slightly attacked by strong mineral acids. It melts down well and has the appearance of the characteristic antimony type of enamel. It will

be noted that these acid-resisting enamels contain added quartz and are quite high in soda. They both contain lead, one being a tin enamel, and the other of the antimony type.

COLORED DRY PROCESS CAST IRON ENAMELS

Since colors have become more popular, there has been a demand for colored dry process cast iron enamels. Practically all colors can be produced, most of them being obtained by additions of color oxides or stains to the regular cover enamels or glazes. For pastel tints the opacifier is partially retained in the composition, but if dark colors are desired, the opacifiers are either omitted or reduced to very small amounts. Excessive opacifier tends to cause a mottled appearance, which may or may not be desired. To produce pure colors with no white present, glazes are used, such as are shown in Table 28. These glazes * do not usually contain lead oxide and are of comparatively simple compositions. Two to three per cent of cobalt oxide in the frit batch gives a dark blue, and four or five per cent of black oxide, a black. These two colors, dark blue and black, usually require colored frits, while other colors are usually made by adding the color oxides at the mill to either the glaze or the white cover enamel frit. For further information on color see page 251.

JEWELRY AND COPPER ENAMELS

The production and use of copper, bronze, and jewelry enamels is a highly specialized field of enameling undertaken by only a relatively few concerns. The enamel surfaces produced must be perfect, but with such high priced ware it is economically practicable to exercise great care.

These enamels are usually made in small batches and are often smelted in covered crucibles. Great care is exercised in the smelting operation, the frit often being re-smelted to develop the greatest possible opacity and to eliminate as much as possible of the dissolved and occluded gases. The enamels are applied to the metal by either the dry or the wet process. In some cases the slip is thin and can be sprayed or dipped onto the ware. In other cases, as with some jewelry enamels, it is more like a paste and is pressed into the spaces to be enameled. Although much of the modern enameled jewelry closely resembles the cloissoné and champlevé ware, which is entirely made by hand, other methods are used. The metal shape is often stamped or cast with the cavities and ridges. The enamel is then filled in between

* Transparent frits are often called glazes.

TABLE 29
JEWELRY AND COPPER ENAMEL COMPOSITIONS

	JEWELRY ENAMELS					COPPER ENAMELS							
	1	2	3	4	5	6	7	8	9	10	11	12	13
Feldspar.....	28.7	1.1	1.1	1.1
Borax.....	6.2	18.6	4.0	3.8
Quartz.....	18.7	18.2	50.0	29.6	16.2	38.0	29.0	30.7	28.9	26.6	27.0	28.6	29.0
Soda ash.....	5.8	3.9	4.2	1.7	1.7	3.8	1.7	2.1	3.4
Soda nitre.....	4.7	2.0	2.4	2.4	2.4	3.8	3.8
Pearl ash.....	2.0	2.0	4.4	2.0
Potash nitre.....	37.5	54.4	15.0	33.2	2.8	2.8	2.1	2.8	3.0	3.0
Red lead.....	37.5	27.3	35.0	37.2	49.7	41.9	44.5	46.6
Barium carbonate.....	6.8
Whiting.....	6.9	0.7
Oryolite.....	6.7
Arsenic oxide.....	5.0	5.1	4.6	4.6	4.9	4.6	5.1	5.1
Tin oxide.....	9.1	9.2	9.4
Boric acid.....	17.0
White lead.....	100.0	54.7	56.5	51.5	58.4
	99.9	99.9	100.0	100.0	100.0	102.0	100.0	100.0	100.0	100.0	100.0	100.1	100.3

MELTED COMPOSITION

	1	2	3	4	5	6	7	8	9	10	11	12	13
Potassium oxide.....	22.9	36.0	7.7	19.0	6.3	3.4	1.5	3.1	3.1	4.5	3.1	1.5	1.5
Sodium oxide.....	1.3	15.0	1.5	5.4	2.1	2.1	2.5	2.1	3.5	3.5
Boric oxide.....	3.0	13.4	1.6	1.5	3.5
Silica.....	24.6	25.9	54.8	36.0	47.8	38.0	31.5	34.8	32.8	30.0	30.8	31.0	31.0
Lead oxide.....	48.2	38.1	37.5	45.0	51.4	44.7	53.5	55.5	50.0	57.5	47.0	45.0
Barium oxide.....	6.7
Calcium oxide.....	5.0	0.4	2.5
Sodium fluoride.....
Aluminum oxide.....	6.8
Aluminum fluoride.....	5.0
Arsenic oxide.....	5.3	5.5	5.2	5.2	5.5	5.2	5.5	5.5
Tin oxide.....	9.9	10.0	10.0
Feldspar.....	1.3	1.3	1.3

these ridges and fired. A polishing operation follows in which the enamel and metal boundaries are ground smooth. A glossing fire then follows and after a light polishing of the metal the ware is finished.

Copper enamels are used quite extensively for telephone dials, small signs, and name plates. A ground coat is usually necessary for these enamels, since there is a tendency for the copper base to be taken into solution in the cover enamels with a green discoloration.

R. R. Danielson and H. P. Reinecker¹⁴ studied copper enamels extensively and state that the melting is a very important operation in the development of opacity, and suggest slow cooling rather than quenching in water. They also state that these enamels are very sensitive to small changes in composition. In their work they found that sodium oxide promotes gloss, but reduces the opacity; lead oxide promotes fusibility without materially reducing the opacity; cryolite is not a desirable flux or opacifier because it tends to develop a matt surface; boric oxide is undesirable in large amounts and is better avoided entirely, and the use of arsenic oxide makes the tin oxide unnecessary.

B. T. Sweeley¹⁵ also studied the relation of the composition and properties of copper enamels and came to the conclusion that the compositions for good enamels should fall within the following limits:

EMPIRICAL FORMULA LIMITS		
.3 — .6 KNaO	1.3 — 1.8	SiO ₂
.7 — .4 PbO	0 — .2	B ₂ O ₃
	0.05 — 0.15	As ₂ O ₃

Table 29 shows the compositions of typical jewelry and copper enamels. Compositions number one, two, three, and four are jewelry enamels containing neither opacifier nor color. It will be noticed that these compositions are essentially potassium lead silicates.

Composition number five is a ground coat for copper enamels recommended by B. T. Sweeley.¹⁶ Its chemical composition resembles a sheet iron ground coat composition to some extent, except that it contains barium carbonate and whiting. In the batch composition the soda and boric oxide are added as soda ash and boric acid instead of borax. A substitution of borax would probably be equally satisfactory.

Compositions six to thirteen inclusive represent a series recommended by Danielson and Reinecker.¹⁷ They are copper enamels and

¹⁴ The Production of Some White Enamels for Copper, J. Am. Ceram. Soc., 4, 827 (1921).

¹⁵ J. Am. Ceram. Soc., 4, 350 (1921).

¹⁶ *Ibid.*

¹⁷ The Production of Some White Enamels for Copper, J. Am. Ceram. Soc., 4, 827 (1921).

are very satisfactory; compositions eight and thirteen having been checked by the author.

Summarizing these compositions for jewelry and copper enamels, the chemical composition shows them to be essentially lead silicate glasses with small additions of the alkalis. They are, in general, opacified with about five and one-half per cent of arsenic oxide.

In some experiments, the author has had considerable success in the enameling of copper with regular sheet iron cover enamels. The opacity of these enamels is not as strong as that of the regular copper enamels, but they have the advantage of cheapness and freedom from lead and arsenic. No ground coat was used, but two coats of the cover enamels were necessary to develop a good white. The compositions in the center of the field illustrated in Figure 62, specifically, numbers five, six, nine, ten, and eleven, were very satisfactory.

CHAPTER 8

Frit Making

Although antiquated methods for making frit are still used in many plants, the more modern concerns have developed highly efficient equipment and methods. The enamel frit manufacturing companies have been foremost in this development and the benefits to the enameling industry have been far reaching.

The mechanical methods of handling the raw materials and protecting them from contamination have been highly developed. The weighing, mixing, smelting, and quenching have been put on a systematic, economical basis. Control has been installed wherever possible and the variation of the product brought to a minimum. Frits of uniform chemical and physical properties are now made for practically every type of enameling, and the plants which are unable to produce their own frits economically can buy them from the larger concerns.

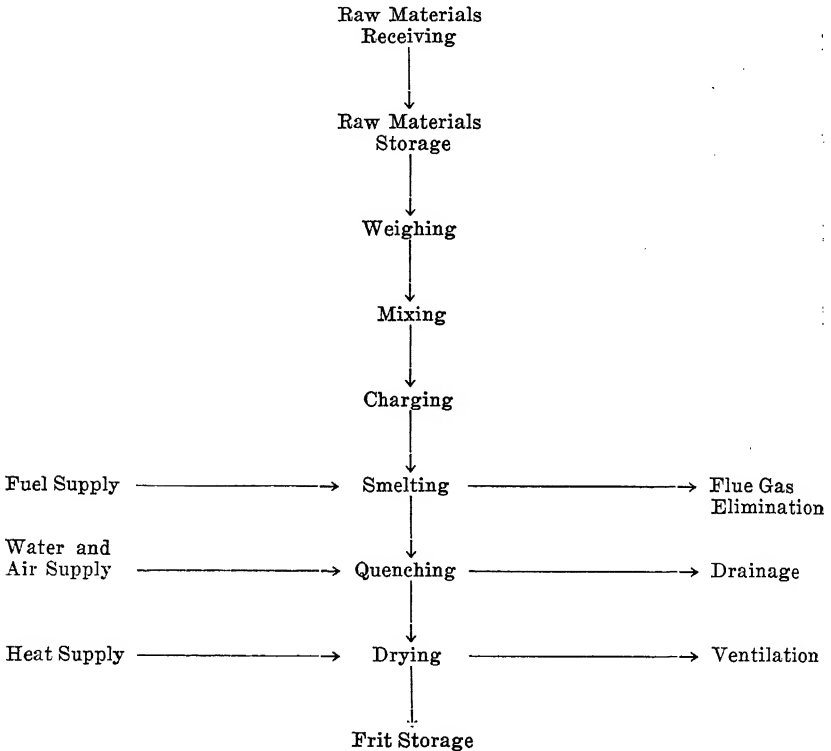
Frit making may be divided into three divisions: raw material preparation, smelting, and frit handling. A flow sheet of the principal operations is shown in Figure 64. Control methods are not shown, but they are essential and will be discussed as each operation is considered. Magnetic separation of iron particles may follow either weighing or drying or both.

Receiving and Storage. The chemical manufacturers have co-operated with the enameler in shipping the raw materials in a manner that will aid his handling. Most of the materials are received in bags or barrels which permit ready mechanical or manual handling and storage. Where the production is large, bins holding one to two carloads are used. These are made in the shape of hoppers, which can be discharged from the bottom where the batch is weighed. Mechanical elevators are used to raise the materials to the charging floor over the bins, and manholes in the floor serve to charge the bins. Such materials as quartz, borax, feldspar, fluorspar, and cryolite can be handled in bulk, provision being made to keep them from "hanging up" in the bins. Most chemicals can be bought to advantage in carload lots, which gives the large consumer quite an advantage. The chemical control of these raw materials, which involves chemical analyses, is also considerably simplified where large shipments are received.

Where the use of bins is not feasible, the bags and barrels are stacked in the storage room where they are convenient for batch-

making. Monorail conveyors are often used to aid the stacking and weighing of these packages. The batch scale itself is often mounted on wheels so that it can be moved from place to place as the different materials are weighed. Where the storage and batch-making equipment are well arranged, it should be possible to make up batches of eight to ten chemicals in about ten minutes.

FIGURE 64
FLOW SHEET FOR FRIT MAKING



In a modern handling and storage department the bins are arranged in a straight line with space below for the batch-making equipment. Such an arrangement aids in keeping the enamel formula secret as it permits the weighing to be done by bin number rather than by material.

The discharge doors of bins used for the raw materials are located at the bottom and must be so constructed as to give perfect control of

the flow. If the material "hangs up" in the bin, it may fall with a rush and, if not controlled, will force itself out through the discharge.

Weighing. The making of the enamel batch requires a careful, dependable, intelligent workman. It is often necessary to intrust this man with the formulæ and few concerns care to have their enamel compositions known to their competitors. To avoid this, numerous methods are resorted to. The use of numbers rather than the names of the raw materials has already been mentioned, but such a method is subject to criticism. A man familiar with the appearances of the different materials can identify them, or they can be identified by simple chemical tests or comparison. The system of making two batches by different men and mixing them together is cumbersome and expensive. If the two men compare notes they can figure the formulæ. The method of weighing the bulk of the batch in the weighing room and a small addition of such constituents as fluorspar, cryolite, and small amounts of the bulk materials in the laboratory is fairly satisfactory. This method is often used and, if modified from time to time, will confuse attempts at solution.

The use of the blind scale or the dial scale without numbers is quite satisfactory, especially if the order of the additions is modified from time to time. This method in conjunction with the method of weighing a part of the batch in the laboratory is probably the most secret method, if the man doing the weighing cannot be trusted with the formulæ.

In some modern installations of weighing equipment the actual weighings are recorded by an automatic recording machine, so that any mistakes or carelessness will be exposed. The recording machine is usually locked to prevent tampering and a violation of the weighing procedure is not permitted. On such records even small variations are readily detected, which, if checked, eliminate the human element from influencing the accuracy of weighing.

The scale is usually built on wheels and is preferably moved along a track, which permits the weighing at each storage bin. If a stationary scale is used, the scale should be set in the floor so that the hopper used for weighing is at a convenient height for the addition of the different materials. Either monorails or trucks are used for bringing the materials to the scale.

The weighing hoppers are usually square or round sheet iron boxes with the bottom tapering to an opening about one foot square, which is closed by a sheet iron sliding door. The hoppers are handled by means of an overhead monorail.

Mixing. The mixing of the raw batch is usually preceded by a coarse screening to break up any lumps of material and to eliminate such refuse as wood, string, cloth, or nails, which may get into the materials from packages. Sometimes an electro-magnet is also used. The simplest method of mixing is that of using a hoe and a box similar to the old method of mixing mortar. The more modern methods are: the use of large cylinders similar to concrete mixers, hexagonal cylinders, or horizontal mixers. The horizontal mixers are generally trough shaped, containing a revolving shaft on which are mounted paddles or spirals to mix the materials. The batch is usually fed into these mixers at one end and discharged at the other. The barrel or concrete mixer types are charged with the batch and rotated for five or ten minutes and then discharged.

The complete mixing of the materials in the batch is very important. Since the batch is made up of refractories and fluxes, the speed of reaction during smelting is dependent on a uniform mixture. If good mixing is not obtained, a longer time is required to smelt the batch, since the rate of reaction is directly proportional to the surface contact, and the more intimate the mixing, the more surfaces of contact exist between the particles of the flux and refractories. Good mixing also aids in the development of uniform color and opacity. Enamel glasses are quite viscous, therefore the distribution of different materials after melting is slow and often incomplete. The fact that all of the materials entering the enamel batch are not of the same size, shape of particles, or specific gravity, makes mixing difficult, but good mixing is a great aid to good smelting and should be attained.

The batch, on discharge from the mixer, is received in a hopper and is then ready for charging to the smelter.

Smelting. Although the literature contains very little on the smelting of enamels, it is a very important operation and one which must be carefully controlled.

Smelting involves the melting together of the raw materials entering the enamel composition until a fairly uniform glass is formed. The successful accomplishment of this result is dependent on the thorough mixing of the raw materials, the proper heating, and the distribution of the heat through the batch. Some of the materials entering the batch are volatile, some fuse readily, some decompose readily, and others are highly refractory. The more fusible materials melt first, giving the batch the characteristic of being wet like slush in a spring thaw, thereby hindering the rapid evolution of gases and the loss of the more volatile constituents. These volatiles become occluded

and absorbed by the melt which takes them and the more refractory materials into solution.

The physical and chemical changes taking place in the smelting of enamels are quite complicated and are not entirely understood. The fundamental changes are, however, the interaction of acids and bases, decomposition, fusion, and solution. The exact nature, the degree, and the order of these changes, however, depend upon many conditions, such as temperature, the combinations of raw materials present, and the agitation.

Even in the early stages of smelting pronounced changes take place in the batch. Sodium nitrate melts first (586° F) forming a mobile liquid dissolving and reacting with the other constituents. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) begins to give up some of its water of crystallization as steam, and melts at about a red heat. This evolution of steam and melting causes a considerable agitation in the batch, which can be observed in the early stages of smelting. The molten borate readily dissolves metal oxides and initiates chemical action among the other constituents. It is quite probable that the presence of the steam itself greatly accelerates the rate of chemical reaction in the batch. If magnesium carbonate is present, it decomposes into carbon dioxide gas and magnesium oxide, which is a strong base. White lead gives up its water and carbon dioxide at about 752° F and red lead a part of its oxygen at 932° F . At temperatures of from 1500 to 1700° F the soda ash and lead oxide melt, and whiting is decomposed into carbon dioxide gas and lime.

The gases being evolved at temperatures up to 1700° F therefore include steam, carbon dioxide, oxygen, and possibly some of the nitrogen oxides from the sodium nitrate which has reacted with the other constituents. The molten soda ash is an active flux at these temperatures, attacking the more acid constituents with the elimination of additional carbon dioxide. The fluorides are soon taken into solution with an evolution of some fluorine and volatile fluorides. The melt becomes more mobile and active with these fluoride additions and increases in its attack on the feldspar and quartz grains. Antimony compounds are either oxidized to antimony pentoxide by the sodium nitrate or they are dissolved in the melt. Other opacifiers, such as tin, and zirconium oxides, are partially dissolved and, if excessively heated, they may be taken entirely into solution. Antimony oxide, unless it is kept oxidized to the pentoxide, melts at 1213° F , a much lower temperature which may account for its ready solution in some melts. The opacity of enamels is very sensitive to the smelting procedure and the

composition of the melt. Tin oxide must be present in the melt as a suspension. Arsenic oxide and the fluorides appear to dissolve in the melt and crystallize out on cooling. Zirconium oxide appears to form an immiscible glass dispersed in the melt, but its nature is not definitely known. Antimony pentoxide must be present as a suspension in the glass. The exact natures of these high temperature phenomena are, however, not known. The use of the X-ray will probably contribute much to our knowledge of them.

In a consideration of the physical and chemical changes of the batch, it is also necessary to study the effect of the furnace refractories and the furnace gases. The refractories used for smelter linings are high alumina clay brick or blocks with a low iron content. The iron content must be low, because the melt rapidly absorbs the iron, causing a green discoloration. If light colored or white enamels are being smelted, the refractories containing appreciable iron contents may cause dark specks in the frit. A highly aluminous refractory (flint fire clay type) is more slowly attacked by the fluxes in the enamel than are those high in silica.

When considering the furnace gases in the smelter, it is again important to return to the frit batch. The enamel batch itself provides a sort of gaseous blanket over its surface, which prevents the furnace gases from affecting it during the early stages of smelting. An enamel, for example, containing 35 per cent of borax and 10 per cent of soda ash loses about 165 pounds of water and 42 pounds of carbon dioxide for every 1000 pounds of frit. This is equivalent to 3290 cubic feet of water vapor at 32° F and a pressure of 29.9 inches of mercury. At a furnace temperature of 1700° F this would be equal to 14,500 cubic feet, or over a period of thirty minutes, about 483 cubic feet per minute or 8 cubic feet per second. With 42 pounds of CO₂ eliminated over the same period, which would be at a rate of one cubic foot per second, there would be a total gas evolution from the enamel of about nine cubic feet per second, disregarding that evolved from the nitrate. This protects the enamel from contact with the fuel gases during the early stage of smelting.

Figure 65 shows the content of carbon dioxide and oxygen in the atmospheres over an enamel batch plotted against time of melting. It is evident from the curves that the carbon dioxide is given off gradually, and also that the sodium nitrate keeps up the oxygen content of the atmosphere.

Rate of Evolution of Carbon Dioxide and Oxygen. It has been shown that atmospheres of carbon dioxide and atmospheres of nitro-

gen up to one hundred per cent are not detrimental to the smelting of enamels.¹ Reducing gases are not detrimental to the smelting of most enamels, although those high in lead may be affected after the completion of the first evolution of gases from the enamel. Under extreme reducing conditions, lead, antimony, and tin compounds may be

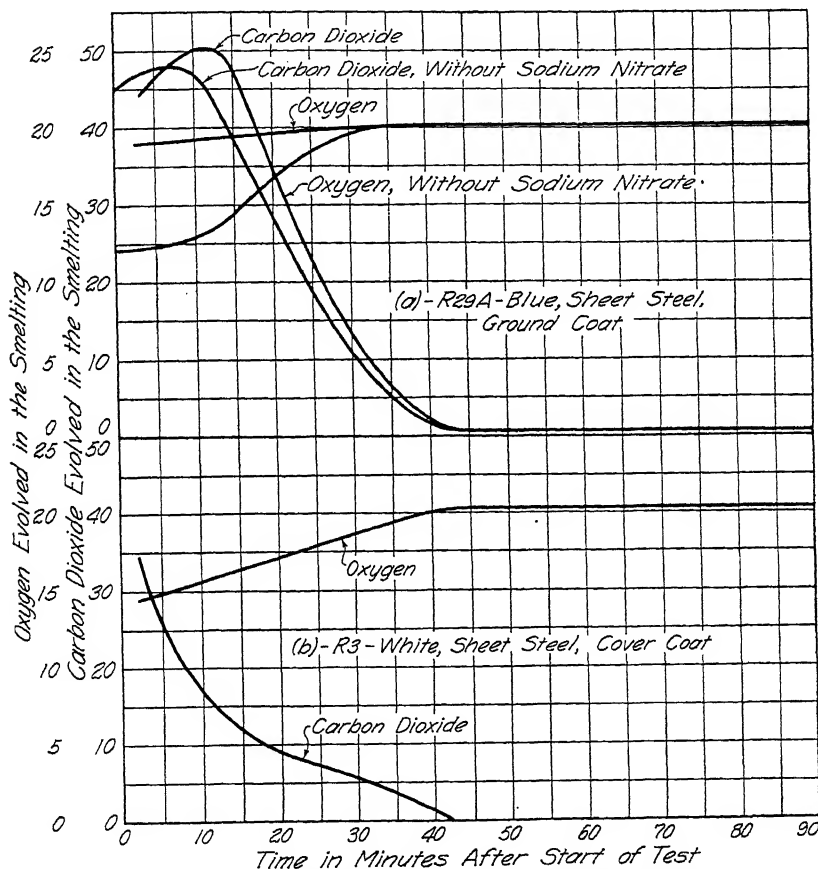


FIGURE 65. Rate of Evolution of Carbon Dioxide and Oxygen with the Furnace Preheated.*

changed to the metallic form, in which case they settle as metallic beads in the bottom of the smelter.

Sulphur oxides in the smelter gases are absorbed by the enamel during smelting, forming an immiscible sulphate melt on the surface, which is soluble in water and is eliminated in the quenching operation.

¹ University of Illinois, Engineering Experiment Station, Bul. 224.

* Ibid.

Dust, dirt, and soot must be avoided in the smelter atmosphere, since solid particles may be caught in the batch and cause specks and blisters in the enamel.

It is evident on considering the nature of these changes that time is an important factor in smelting enamels. Heat applied too slowly will not give ideal conditions, because the first melt formed will then react only very slowly with the most refractory constituents, consuming excessive time and causing a loss of efficiency. A temperature sufficient to vaporize these more fusible materials might not be high enough to volatilize them, if they were in chemical combination with the more refractory constituents. By holding the low temperature for a long period of time, these original fluxes would be gradually vaporized. The loss of efficiency, however, because of the low production of the equipment when smelting at excessively low temperatures, makes this practice very uncommon.

Since a rapid application of heat results in increased production, it is a common fault in smelting. If the enamel batch is heated too rapidly, the more fusible constituents are melted and volatilized before they have a chance to react with the more refractory materials. This results in a final batch, which is harder (less fusible) than it would have been if less of the fluxes had been driven off. Excessive smelting, after the melt is ready to pour, results in a similar condition and, if carried on long enough, necessitates a further increase of temperature to permit pouring.

Enamel batches vary considerably in their smelting characteristics, so that a careful study of each composition is necessary to determine the best temperature and time for proper smelting. There is considerable latitude in these conditions, but for each type of enamel and equipment there is a combination producing the best frit with the greatest economy.

Enamel ground coats are usually smelted much harder than cover enamels. The sheet iron ground coats are generally smelted until they are free from bubbles and particles of unfused material. They are smelted to a fairly uniform glass, but must not be heated too long and at too high a temperature or they become brittle. Dry process cast iron ground coats are viscous and refractory and are seldom melted to a good glass. They contain bubbles, but the less fusible constituents are generally entirely taken into solution. They are poured in a viscous condition, no attempt being made to heat them to a mobile melt. If over-smelted they, like the sheet iron ground coats, become brittle and refractory.

Most copper enamels contain opacifiers, which must not be taken into solution during the melting operation. These opacifiers serve their purpose only when they appear in the frit as inclusions uniformly

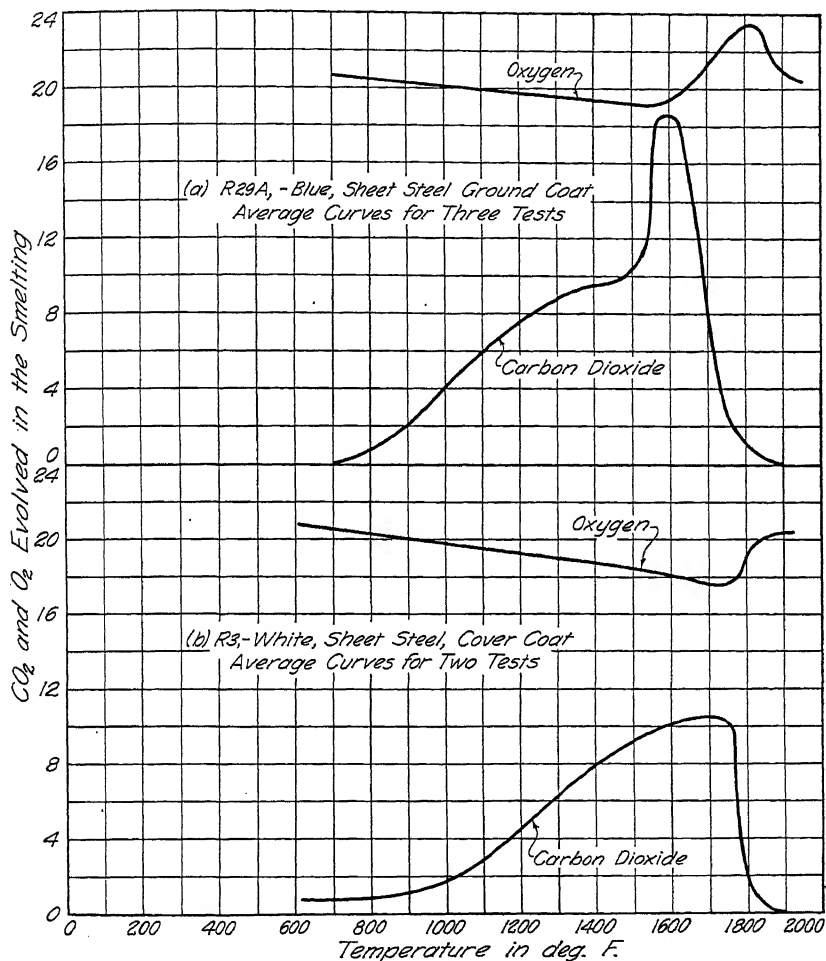


FIGURE 66. Rate of Evolution of Carbon Dioxide and Oxygen Heating from Room Temperature.*

dispersed in the matrix of glass. In some cases they dissolve in the melt and recrystallize on cooling, while in others they are present in the molten glass as immiscible melts or solids. Cover enamels must in general be smelted much more carefully than ground coats to avoid the

* *Ibid.*

loss of opacity. Enamels containing antimony compounds as the opacifiers are not smelted until they form a smooth thread; they are only smelted until the bubbling ceases. Since dry process cast iron enamels depend entirely upon the frit for their opacity, they are even more sensitive than the wet process types.

- ✓ Many defects of enamels have their origin in the smelting operation. Insufficient smelting may cause blistering, loss of weather or acid resistance, poor gloss, and poor texture in the finished enamel. Over-smelting may cause loss of opacity, fishscale, poor gloss, refractoriness, and discoloration. The color and opacity of many cover enamel frits are sensitive to the degree of smelting. In some white enamels a distinct blue develops and in others, shades from yellow white to blue white.

In some enamel compositions, especially those containing lead, antimony, or tin compounds, reducing conditions in the smelting atmospheres may cause serious defects. These defects are usually present as brown or black specks in the enamel frit, but in extreme cases they consist of metallic beads in the bottom of the smelter. These specks, however, must not be confused with those arising from contamination by dirt in the raw materials, or those getting into the enamel from careless practice. It is possible for dirt specks to get into the enamel from the fuel and the air used in smelting.

Quenching. The principal object of quenching the molten enamel is to facilitate grinding. If the glass is slowly cooled it forms hard lumps, which are difficult to crush or grind. It is, therefore, important to obtain as complete and uniform quenching as possible. The milling of poorly quenched frit requires much more time than that properly quenched. A non-uniform quenching procedure results in a non-uniform product and considerable variation in the milling times and efficiency.

Molten enamel poured into water is chilled only on the surface, a layer of steam forming over it, which prevents rapid cooling. Chunks of frit will, therefore, remain hot for considerable periods of time and will not be shattered. If the fluid molten enamel passes through a blast of air and water, it is broken up into small droplets and threads, which, as they strike the water, are quickly cooled, causing them to shatter because of the strains set up in the glass. A good frit is not only broken into small pieces, but each piece is intersected with cracks, which make further reduction of size quite easy. In the interest of reduced cost of milling (an expensive operation), the frit should be thoroughly shattered.

Attempts have been made to quench the molten enamel by blowing it with air alone into a large chamber. Reports of this method claim a

better product than that of the air-water quench, but the trade has not adopted the method. It involves considerable space for quenching, careful control, and greatly increased storage space. The frit formed by air quenching is fluffy and for a given weight occupies much more space than the air-water quenched frit. It is claimed, however, that it is much more easily ground and that the product has better opacity and better acid resistance.²

Drying. After quenching, frits may or may not be dried, depending upon the operations to follow. If the frit is to be milled wet, it is sometimes charged to the mill without drying, but in such cases the water content should be determined. Frit which has been drained and allowed to stand in the air may contain from five to fifteen per cent water. This amount of variation will affect the milling and the properties of the slip to a great extent; therefore, if the frit is added to the mill in the wet condition, a correction for the water content should be made.

Three different types of equipment are used for drying frit: the drying table, the stationary dryer, and the rotary dryer.

The drying table is a flat hearth on which the wet frit is dumped. Heat is applied from beneath the hearth and the frit is raked by hand to accelerate the drying. This method is crude and wasteful of fuel, unless waste heat is used. The frit is subjected to contamination by settling dust and considerable labor is required for handling.

The stationary type of frit dryer is usually a sheet iron chamber into which the basket of frit is placed. The air used for drying the frit is heated by passing it through an interchanger on the flue of the smelters. This air is passed down through the basket of frit and is then exhausted into the flue. The method is desirable, because it utilizes waste heat and clean air can be used, thus avoiding the danger of contamination.

The rotary method consists of dumping the frit into a rotating cylinder. The cylinder is usually lined with porcelain and tilted slightly to one end, causing the frit to move through it continuously. A convenient size is about two feet in diameter and twenty feet long. Air warmed from the waste heat of the smelters moves slowly from the lower end of the cylinder over the frit to the upper end, where it enters a stack. The frit is charged at the upper end of the cylinder and is continually agitated as the cylinder rotates. The dry frit is discharged at the lower end. This method of drying frit is economical and effi-

² A. Malinovsky, *Method of Cooling Enamel by Compressed Air*, J. Amer. Ceram. Soc., 6, 972-3 (1923), and Stefan Wiester, *Air Cooled vs. Water Quenched Enamels*, J. Amer. Ceram. Soc., 6, 973-4 (1923).

ent. The frit is protected from contamination and in addition is broken up slightly by the motion. If the frit is to be screened to give it a more uniform size for milling, it has the advantage of a preliminary preparation for the screens.

In some plants, particularly those supplying frit to the market, magnetic separation of iron-bearing impurities in the frit is becoming quite popular. Regardless of the care exercised in manufacture, particles of iron or iron-bearing slag may get into the frit and, if not removed, they produce black specks in the enamel.

TABLE 30
DECOMPOSITION AND FUSION PROPERTIES

MATERIAL	FORMULA	DECOMPOSITION		MELTING TEMP.	
		Product	°F.	°C.	°F.
Feldspar.....	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	1170	2138
Borax.....	$Na_2B_4O_7 \cdot 10H_2O$	$Na_2B_4O_7$ & H_2O	167	741	1366
Quartz.....	SiO_2	1710	3110
Fluorspar.....	CaF_2	1360	2480
Cryolite.....	Na_3AlF_6	1000	1832
Soda ash.....	Na_2CO_3	gradual	851	1564
Soda nitre.....	$NaNO_3$	gradual	308	586
Red lead.....	Pb_3O_4	PbO & O_2	932	888	1630
White lead.....	$2PbCO_3 \cdot Pb(OH)_2$	PbO , CO_2 & H_2O	752	888	1630
Litharge.....	PbO	888	1630
Barium carbonate.....	$BaCO_3$	BaO	2642	1923	3493
Whiting.....	$CaCO_3$	CaO & CO_2	1517	2570	4653
Magnesium carbonate	$MgCO_3$	MgO & CO_2	662	2800	5072
Zinc oxide.....	ZnO	> 1800	> 3272
Antimony oxide.....	Sb_2O_3	Sb_2O_3	1654	1550	2822
Sodium antimonate.....	$NaSbO_3$
Zirconium oxide.....	ZrO_2	2700	4892
Titanium oxide.....	TiO_2	1640	2984
Sodium silicate.....	Na_2SiO_3	782-1080
Cobalt oxide.....	Co_3O_4	Co_2O_3 , CoO , Co & O
Manganese oxide.....	MnO_2	MnO & O	995	1650	3002

The magnetic separator usually consists of a belt on which the frit travels and auxiliary belts, behind which electro-magnets are located. As the frit on the conveyor belt passes these magnets, the iron particles or even particles of frit containing small amounts of iron are drawn to the magnetic belts. These belts convey the magnetic material away from the batch and drop it in a container at one side. The frit passes to the frit storage or the hoppers for use.

SMELTERS

Three different types of furnaces are used for the smelting of vitreous enamels: crucible or pot furnaces, hearth (box) type furnaces, and rotary furnaces.

Crucible furnaces are used only where the batches are small, as in

the making of jewelry enamels, in laboratory tests, and in making special colors. Although this type of furnace is not economical of fuel, it has advantages for special work. The enamel batch smelted in a crucible can be kept out of contact with furnace gases and, where desirable, can be covered. In the making of jewelry enamels containing arsenic oxide, the covered crucible prevents excessive loss of this volatile oxide and the accompanying danger from the poisonous fumes.

The Crucible Type. The crucible type furnaces are usually fired with gas or oil, but can be heated by electricity. The combustion chamber in the gas and oil furnaces surrounds the crucible. The electric furnace is of the resistance type, the elements being placed vertically around the crucible. The refractory and fuel costs are high, since the heat must pass through the crucible to the batch.

In the operation of the crucible furnace the well mixed batch is charged into the hot crucible, and, toward the end of the smelting, it is stirred with a clean iron rod. Samples are taken and threads drawn from time to time to determine the progress of smelting. When thoroughly smelted the melt is poured in a fine stream into cold water, shattering the frit. With some enamels containing arsenic oxide the melt is poured on a flat plate, because better opacity is sometimes obtained with slow cooling. Figures 67 and 68 show diagrams of a gas-fired crucible smelter and a rotary smelter.

The Hearth Type Smelter. The hearth type smelter has for many years been the most common type of furnace used for making enamels. This type of smelter has the advantage of simple construction, fairly efficient operation, and long life. It can be easily insulated, and the refractory lining can be readily replaced when badly worn. The design of this type of smelter varies considerably from one plant to another. It consists essentially of a refractory box or tank (Figure 69) with the bottom sloping to a point near one side, where the tap hole is located. The side walls support a crown, which extends over the furnace. Brick and insulation are built around this with steel rods and clamps holding it in shape. The modern furnaces are fired with fuel oil or gas, the flame being so adjusted that it passes over the surface of the enamel batch. The burner or burners are placed at one end with the flue at the opposite end. In the smaller furnaces of this type one burner is sufficient, but in the larger type two or more are used. The batch is charged through a hole in the crown of the furnace and is leveled out with a rod or rake through a port hole in the side. The discharge is through the tap hole at one side in the floor. These furnaces vary in size from the fifty-pound laboratory smelter to the large commercial

types smelting several thousand pounds. An 800-1000 pound smelter is a common size in most plants. The smelters are often built in pairs having one side common to the two.

The ordinary hearth sizes of these smelters are 22 x 30 inches for 100 pound batches, 5 x 7 foot for 1000 to 1200 pound batches of raw material, and the 6 x 8 or 7 x 9 foot sizes used for dry process enamels.

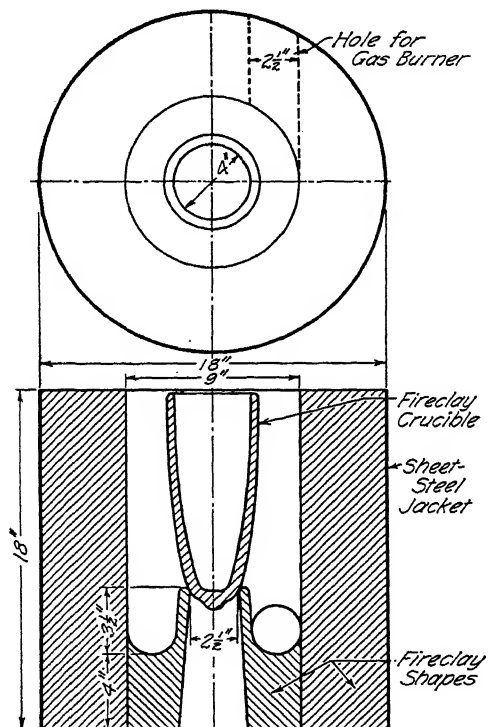


FIGURE 67. Crucible Smelter.*

These larger smelters will take batches of 2500 or 3500 pounds. The general rule, as given by F. M. Burt,³ for the capacity of smelters is that for sheet iron frit 25 to 35 pounds of batch can be smelted for each square foot of hearth area. Also 30 to 40 pounds of wet process cast iron enamels or 45 to 50 pounds of dry process cast iron frit can be produced for each square foot of hearth area.

* A. I. Andrews, *Uni. of Ill., Eng. Exp. Sta., Bul. 201* (1930).

³ *Ceram. Ind.*, 16, 381 (1931).

The hearth of these box type smelters usually has a slope toward the tap hole of one inch in two or three feet. The curb wall is built around this hearth, the blocks extending three or four inches below the surface of the hearth. An upper course of curb wall brick is built on this and around the outside; a wall of nine-inch straights runs two feet above the hearth to support the crown, which is also made of stan-



FIGURE 68. Commercial Smelting Room.*

dard fire clay bricks. The selection of the refractories to be used in smelters is an important consideration, a good grade of high aluminous fire clay usually being considered preferable.

When gas is used as the fuel, several burners are usually employed at one end of the smelter. The proportional type mixer burner is generally used, and the burner fits closely into the wall of the smelter, no auxiliary air being used. These burners may be of either the type using fifteen to twenty pounds of gas and the appropriate amount of air to give good combustion, or of the inspiration type. In the latter type the gas is under a low pressure and is inspired into the burner by the flow of compressed air or gas through a venturi.

* Courtesy of the Titanium Alloy Manufacturing Co.

If oil is used as fuel, one burner is usually sufficient. The oil flame is very long, which in some cases necessitates the installation of the oil burner at the same end of the smelter as the flue. The flame then travels the length of the smelter and returns to the flue. By proper operation very little short-circuiting is encountered and the temperature distribution is good.

Most smelters are equipped with pyrometers of the thermocouple type. The location of these is an important consideration and, once the most desirable smelting temperature conditions are obtained, they should be strictly adhered to. The furnace temperature for sheet iron ground coats is usually 2050 to 2200° F, for white cover or color enamels 1900 to 2100° F, for special hard enamels and one coat grays

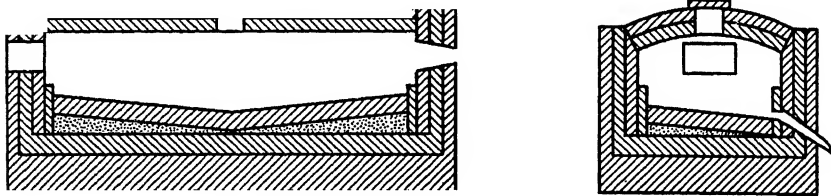


FIGURE 69. Hearth Smelter.

2500° F, and for dry process cast iron enamels 1900 to 2100° F. It is doubtful, however, if the enamel itself ever exceeds a temperature of 2100° F, although the furnace temperature is much higher. The temperature and time of smelting must, however, be determined for each enamel composition. Some enamels require rapid smelting at high temperatures, while others require a low temperature over a longer period of time. The conditions for each enamel composition should be determined and standardized, otherwise the properties of the frit will vary considerably.

The heat in the flue gases can be used to preheat the incoming air, to dry the enamel frit, or to heat the smelter room. An interchanger is often used for this purpose, thus eliminating the objectionable flue gases.

A pit is generally built on the side of the furnace under the tap hole. This pit contains a tank filled with water and a monel metal basket just fitting the inside of the tank and large enough to receive one charge of frit. As the molten enamel flows off the end of the trough under the tap hole, it is usually blown into the tank by means of a spray of water and air which aids greatly in breaking up the frit. The basket

is then raised out of the tank of water and drained, after which it is transferred to the dryer and finally to the frit storage bin.

Operation. The box type of smelter is brought up to temperature before the batch is charged into it. This requires many hours, therefore the smelter is usually run continuously, one batch following another until a considerable quantity of frit has been accumulated.

Before charging the batch into a smelter, the burners are turned off and the flue closed to prevent the dust from being carried up the flue. The batch is charged from a hopper through the door in the crown and leveled off by means of an iron rod or hoe. The flue is then re-opened and the burners are lighted.

(The batch melts from the surface down, although considerable heat is obtained from the hot hearth.) As the heat penetrates the batch, the borax gives up its water as steam, causing an agitation, which aids the mixing of the batch. Later the decomposition of the carbonates contributes to this and the batch passes through the stages of a solid powder to a mush and, finally, a mobile melt. As it approaches the melt stage, it bubbles violently and then subsides to a quiet liquid. It is usually stirred with an iron rod at some time during these last stages of the operation to make it more homogeneous and to aid the temperature distribution.

Several methods are used to determine when the enamel is completely smelted. The *thread test* is most common. A thread of glass is drawn from the melt and examined. Sheet iron ground coats are smelted to a condition where the thread is free of air inclusions or unfused material. Cover enamels may not be fired beyond the disappearance of the entrapped bubbles. The operator becomes very proficient in judging the degree of smelting by the appearance of this thread.

Sometimes a sample is analyzed for silica as a check on the operator's estimate. High silica content, other things being equal, indicates over-smelting, and low silica, under-smelting. The use of phenolphthalein indicator on the crushed and screened frit is quite common in some cases. If the enamel is under-smelted, the phenolphthalein turns red quite promptly, while, if the enamel is over-smelted, the reaction is much slower. This change is dependent on the solubility of the alkalis of the frit and is suitable only for certain compositions, such as those used for gray ware kitchen utensils.

It is customary to gather a portion of the melt in a shovel as it runs out of the tap hole. The sample is allowed to cool and is then broken

and examined and often kept as a record. The fracture should be smooth and free from both air bubbles and unfused material.

When the smelting is completed, the tap hole is opened and the melt allowed to flow down the spout into the path of the air-water spray and into the basket in the water tank. The frit in the basket is usually stirred to prevent its collecting in lumps and to insure thorough quenching. The operator uses a steel rod to loosen any enamel which tends to cool and adhere to the spout. When removing the wad of clay in the tap hole, the dirt and first enamel passing over the spout are caught in a shovel and discarded. When the enamel ceases to flow, a new wad of clay is put in the tap hole and another batch of raw materials is charged into the smelter. The basket of frit is then raised out of the water tank, allowed to drain, and transferred to the dryer.

The operation of the smelter requires control of the temperature, the products of combustion, and the frit batch.

The temperature is usually controlled by means of the thermocouple installed in the smelter and the hand adjustment of the burners. It is possible, however, to use automatic control for this. Either the thermocouple or radiation pyrometer can be used to actuate the equipment for operating the burner adjustment. The hand adjustment is, however, necessary in some cases (particularly with the rotary type smelter) and in such cases a definite schedule should be followed.

It is possible to adjust the air and gas pressures of the smelter so that, not only will the combustion be most efficient, but a definite temperature can be produced. The upper curve in Figure 70 is derived by plotting the gas pressure against the air pressure for conditions of most efficient combustion. The other curves represent the corresponding data for different percentages of excess oxygen, as indicated. When the temperatures produced in a given furnace have been experimentally determined, they can be noted along these curves and, if a given temperature and given excess oxygen are required, the pressure of the gas and air can be set to reproduce them.

By making Orsat gas analyses of the products of combustion in the stack with different adjustments at the burner, data can be obtained which are valuable in the control of the burners.

The Rotary Type. The rotary smelter is cylindrical in shape and is mounted so that it can be rotated and also tilted. The ends are made conical to retain the batch while rotating. An opening in one end serves for the burner and an opening in the opposite end serves as a flue. A diagram of the American type of rotary smelter is shown in Figure 71. The rotary smelter is built with a sheet steel jacket and

lined with special refractory shapes. It rotates in either direction and can be tilted to a vertical position for pouring the molten enamel. It can be fired with either oil or gas (city, natural, or butane) and is built in various sizes to take from 60 to 1100 pounds of enamel batch. Table 31 shows the dimensions, capacities, and approximate fuel consumptions of these furnaces.

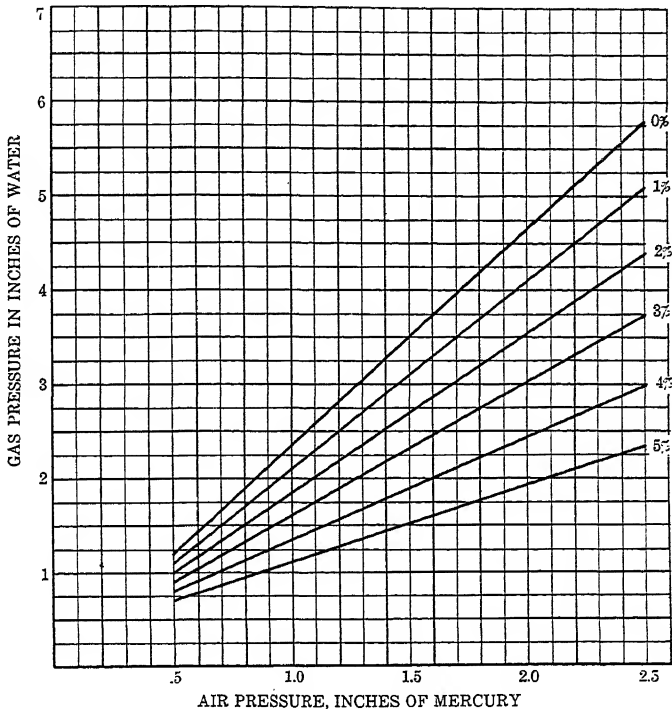


FIGURE 70. Air-Gas Pressure Relation in a Smelter.*

Operation. The rotary smelter is best charged by means of a screw type charger which can reach through the door to the back end of the furnace and deposit the batch as it is withdrawn. It is possible, however, to shovel the batch into the furnace, but in any case it must be distributed to avoid blocking the path of the flame. The charging is always made through the burner opening into the hot furnace. The burner is then swung into place and lighted. The smelter is rotated only far enough to bring the batch up on one side so that the material, as it melts, can roll down to the bottom of the smelter. This subjects new batch constantly to the flame and gives maximum speed in

* W. G. Martin. A. O. Smith Corp.

smelting. The unmelted material is raised up the side by rotating the furnace slightly at frequent intervals. When the batch has practically all rolled down, the furnace is rotated half around, bringing the enamel melt into contact with the hot crown which is then under it. This causes violent boiling and the enamel fines rapidly, after which it quiets down. The furnace is then rotated constantly, which mixes the molten enamel. It is generally necessary, however, to stir the enamel from front to back of the furnace with a steel rod. As the melt ceases

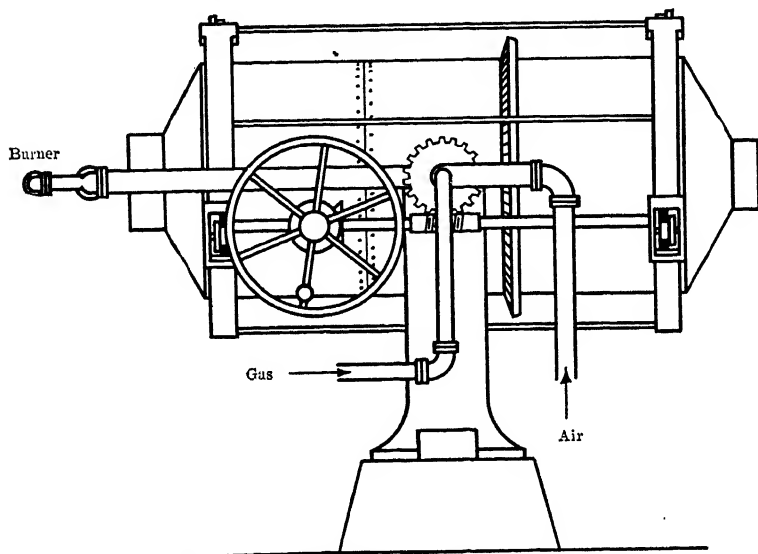


FIGURE 71. Rotary Smelter.

to bubble, samples are taken, and when completely smelted, it is poured.

Pouring is accomplished by tilting the furnace with or without the burner in operation. It is tilted by means of a crank on one side and can be controlled perfectly by one man. The melt is best poured slowly to permit good quenching as the stream passes through the air-water spray and into the Monel metal basket resting in the water tank under the smelter. A very convenient quenching arrangement consists in forcing the enamel frit down an incline, around a curve, and into the frit basket. This agitation makes the shattering of the glass more complete and produces a uniformly fine product.

The rotary type of smelter has an advantage over the box type in that it gives a better mixing of the batch and can, therefore, smelt the

enamel more rapidly. It is economical of floor space and labor, one man being able to operate several smelters. The charge can be readily observed through the door, although this advantage is lost when an auxiliary door is used to increase the economy of the furnace. The charging and pouring can be rapidly done and easily controlled. The rotary smelter has a large fuel consumption and there is no convenient method of automatic temperature recording or control. An optical pyrometer sighted on the batch is generally used to measure the temperature.

TABLE 31
SPECIFICATIONS OF U. S. ROTARY ENAMEL SMELTING FURNACES

	<i>No. 1 Furnace</i>	<i>No. 2 Furnace</i>	<i>No. 3 Furnace</i>	<i>No. 4 Furnace</i>	<i>No. 5 Furnace</i>
Enamel Capacity	60 lbs.	150 lbs.	350 lbs.	750 lbs.	1100 lbs.
Melting Time	30 min.	45 min.	1 hr.	1¼ hr.	1½ hr.
Size Charging Hole	8"	8"	10"	16"	16"
Size Pouring Hole	4"	5"	8"	10"	10"
Shipping Weight	2100 lbs.	3380 lbs.	6725 lbs.	10,930 lbs.	13,400 lbs.
Floor Space	7' x 7'	8' x 8'	10' x 10'	12' x 11'	12' x 13'
Head Room	9'	10'	13'	15'	20'
Approximate Oil per Hour	6 gal.	9 gal.	17 gal.	25 gal.	30 gal.
Approximate Gas per Hour	900	1500	2500	5,000	6,000
Connersville Blower	No. 35-B	No. 40-B	No. 50-B	No. 60-B	No. 60-B
Motor for Rotating	¾ H.P.	½ H.P.	¾ H.P.	1 H.P.	2 H.P.
Inside Diameter Chamber	13¾"	17¾"	25"	33"	33"
Thickness, Fire Brick	3"	4½"	5"	5½"	5½"
Capacity Cubic Inches	585	1785	5138	9500	14,750

Figures are approximate.

While the box type furnace requires many hours to bring it up to a smelting temperature, the rotary type can be heated in a very short time. This is very convenient where intermittent smelting is done. The original cost of the box type smelter is less than that of the rotary, the preference for one or the other type depending upon local conditions.

The relining of either type of smelter requires first-class refractories which fit closely in the furnace. Joints should be made as thin as possible, fire clay being used as the bond. The fire clay is preferably the same as that used in making the bricks. The early smelters were built with large blocks (6" x 14" x 30" or 6" x 12" x 24") to avoid joints, but the more modern types use either small blocks (2½" x 6" x 13½", 4" x 6" x 13½", or 5" x 9" x 9") or standard bricks. The

large blocks are made by hand and are objectionable because of their expense and their low density. The machine-made dry pressed standard shapes are much denser and will withstand the fluxing of the enamel melt much better than the hand-made product. A good flint fire clay refractory (high in alumina) is generally considered to be most satisfactory. Clays with a high silica content do not withstand the fluxing action of the enamel. The refractory used should have a fusion point (P. C. E.) of cone 32 to cone 33, or 3092° to 3173° F. The porosity should not greatly exceed eight per cent and the brick should be burned uniformly to cone ten or eleven. Brick for smelter purposes should not contain iron slag inclusions or specks, since these are readily absorbed by the enamel batch. Light colored refractories are much less objectionable than dark from the standpoint of contamination.

The lining of a rotary type smelter has an average life of about 350 melts, but in some cases it lasts much longer, possibly 600 and rarely 700 melts. The lining of a batch type smelter will last from 1000 to 2400 melts, the curb walls being repaired or replaced as necessity requires. Enamels of the sheet iron type are least destructive to the smelter hearth, while those of the high-lead type attack the refractory quite rapidly.

Most frit manufacturing plants are equipped with a number of smelters, since colored and white compositions cannot be made in the same smelters. The ground coats, blue, and black colors are usually made in the same smelters, while the white opaque enamels and the glazes are made in others.

Ventilation. The smelting furnace room should be well ventilated, because some of the fumes from the enamel practically always escape even with good flue systems. The fluorine gases, lead vapors, and dust are detrimental to health and should be reduced to a minimum. With rotary smelters hoods are often built over the top of the entire smelter to draw off any escaping gases. The frit-making rooms should always be kept clean, for dust accumulating on the floor or equipment leads to contamination of the frit and causes defects in the finished enamel difficult to trace to their source.

CHAPTER 9

Milling and Mill Additions

The milling of enamels is an operation requiring careful control, since it affects the working properties of the enamel and the quality of the finished ware. It involves not only the reduction of the size of the particles, but the accomplishment of this without injurious contamination, and in a manner which can be duplicated from one batch to another. Vitreous enamels are practically always ground in ball mills and usually in those of the batch type.

Although practically all enamels are required to pass a No. 60 to No. 100 sieve, the percentage of fines varies over a considerable range. The specifications for the milled enamels, therefore, generally call for a certain per cent of residue on a somewhat finer sieve. The milling operation must be so controlled as to produce a usable product, because it is not practicable to screen out the excessive fines or any great amount of the over-sized material.

In the milling of white or light-colored enamels, special care is necessary to avoid contamination by dark-colored materials. All enamels must be kept free from refractory materials, which will show as lumps or specks in the enamel coating, and foreign materials, which tend to react with the enamel glass or form bubbles and blisters. This problem of avoiding contamination is very serious, since there are many places where dirt may get into the batch. The raw materials, the water, the air, and even the equipment used for handling and milling must be constantly checked.

The operation of the milling equipment is of primary importance in the control of the product, but good equipment and satisfactory accessories for control are essential to good operation. Poor or inadequate equipment greatly handicaps the operation and is not usually an economy. The greatest efficiency is obtained when the mill room is properly equipped. If the mills used for white enamels are also used for colors, a considerable amount of labor, time, and materials is necessary in cleaning the mills after each change and the hazard of contamination is greatly increased. Frequently it is desirable to have separate mills for different colors. The capacity of the mills used should be adapted to the scale of operations, for an over- or under-sized batch in a mill is ground very inefficiently. Usually several sizes of

mills are desirable to accommodate the different enamels, which are used in different amounts.

In the milling of wet enamels the fineness of the materials influences the colloidal behavior of the slip. The suspension of the slip and its working properties are dependent upon the colloidal content, whether this be added as clay or formed in the milling operation. The properties of these colloids are influenced by the soluble content of the liquor, which may be of either added or accidental origin. All frits are soluble to a certain degree and this soluble material not only affects the colloidal properties, but it influences the activity of added electrolytes, such as borax and magnesium sulphate.

FUNDAMENTAL CONSIDERATIONS

The theories and the operation of ball mills have received considerable investigation, therefore the facts are fairly well known. This has made possible the standardization of ball mill practice and has resulted in reliable methods of operation and control.

As a ball mill revolves, the balls and the batch are carried up the side of the mill by friction, and then either allowed to slip back as a mass, roll, or cascade over into the interior of the mill. Although the size of the batch, the amount and size as well as the distribution of the sizes of the balls, the water content, and other less important factors affect this, the peripheral speed of the mill is of primary importance. The peripheral speed is the rate of movement of the inside of the lining of the mill, a value depending on both the size of the mill and the speed of rotation. With a given speed of rotation the peripheral speed increases with an increase in the inside diameter of the mill. It is, therefore, evident that large mills should not revolve as fast as small mills.

At one time it was believed that the grinding in a ball mill was due to the falling stream of balls from the upper part of the mill to the base, thus crushing the particles by impact, but more recent researches have shown this to be untrue. The slipping of the batch as a whole is likewise inadequate for efficient milling and in addition it subjects the mill lining to undue wear. The greatest amount of milling is accomplished when a churning motion is taking place; this is the condition in which the greatest number of balls are moving over one another, resulting in the maximum number of grinding surfaces. The churning is at a maximum at the toe of the charge, but should take place throughout the whole mass. The grinding in this condition is greatest between the balls, and at a minimum between the balls and the lining of the mill.

These different conditions can be controlled by regulating the speed of rotation of the mill. Figure 72 illustrates the conditions of the batch at different speeds.

Figure 72A shows the condition in a mill which is running at too great a speed. In this condition there is no grinding, the balls and the batch being thrown by centrifugal force to the wall of the mill, where they remain stationary with relation to each other and the mill. At this

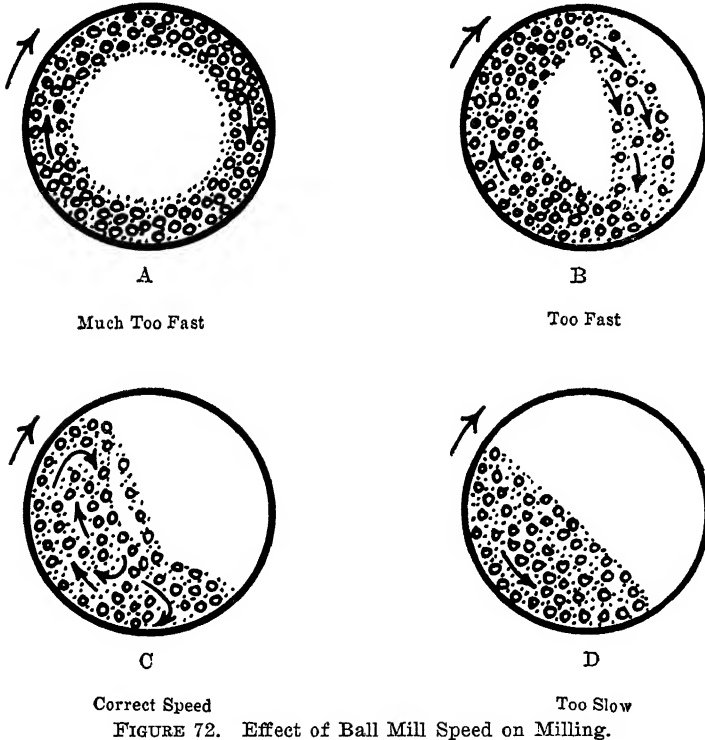


FIGURE 72. Effect of Ball Mill Speed on Milling.

speed there is no noise caused by the balls and the mill runs very quietly.

Figure 72B shows the condition of a mill which is run slower than in Figure 72A, but still too fast for most efficient grinding, a condition common in many plants. The balls are usually broken at an excessive rate, the lining wears away rapidly and the mill is excessively noisy. In this condition the balls are being thrown over the batch against the far side of the mill where they strike the lining without doing work on the material being ground.

Figure 72C shows the condition of a mill being operated at the most economical speed. None of the balls are being thrown over the batch against the mill lining and all of the balls are moving over one another, each doing its share of the grinding. In this condition the batch is uniformly mixed with the balls; the balls are not thrown forcibly against one another, and the mill lining is not abused.

Figure 72D shows the condition when the mill is being operated too slowly. Here there is not enough force exerted to throw the batch over and it slides on the interior of the mill causing excessive wear of the lining with very poor efficiency in grinding. In this condition, the batch can usually be heard to slide periodically as it is carried up the side of the mill. Such operation results in excessive heating and the milling is very slow.

There are all variations in the conditions from the slow to the proper to the excessive speeds. Between the slow speed and the proper speed the batch tends to segregate in the middle of the mass, thus giving reduced efficiency. A slightly excessive speed is preferable to one which is too slow.

The Charge. In milling enamels, the greatest efficiency is attained, if the mills are one-half full of balls. The charge of frit and raw materials added on top of the balls should fill the mill three-quarters full, the water being added last. After milling, the powder or slip should come just to the top of the balls, the mill being about two-thirds full. Mills are generally rated by the manufacturer for a given weight of sand. By multiplying this rating by 0.8 an approximation is obtained for the weight of enamel which can be handled in any given mill.

If too few or too many balls are added, the milling operation will not be efficient. Too few balls permit too much material to collect between the balls which acts with a cushioning effect, resulting in very little grinding. The slip or powder should just cover the balls so as to form a layer between them, so that, whenever the balls come together, grinding can be accomplished. If too few balls are present, a condition exists similar to that when the batch is too large, thus allowing too much material to exist between the balls.

An excess of balls takes up, either space which should be used by the batch, or grinding space, which would permit freedom of motion. In production the fault of too few balls is more common than an excess, as the balls wear away in use and, unless they are systematically replenished, the total grinding surface is gradually lessened. Some operators

periodically examine and reweigh the balls, while others add a few pounds each day to take care of the decrease due to wear.

The amount of the batch should not be varied but should be kept at the optimum for efficient grinding. A large charge of material requires an excessive time for milling and the resulting product will have a different distribution of fines than one of normal amount. There is nothing gained in production by overloading the mill. A small batch will mill very rapidly, but again the distribution of fines will change, resulting in an enamel of quite different properties. In addition, a small batch is very hard on the mill, because the balls pound against each other and the mill lining, resulting in great wear. An undercharged mill will wear itself to pieces very rapidly. An empty mill, that is, one containing only balls or balls and water, should never be run for more than a few revolutions; five or ten minutes of such operation will do more damage to the mill than many days of ordinary use.

The best mill practice is of a uniform character, where the weight of the batch is kept constant, the water constant, the amount of balls constant, the electrolyte constant, and the time or number of revolutions as constant as is consistent with uniform fineness. However well these variables may be controlled, the milling will vary from one batch to another. Such conditions as the temperature, which affects the volumes and the solubilities, will have an influence. With operation the mill lining wears away and increases the diameter of the interior of the mill. It is often necessary with such wear to increase the size of the batch to offset the effect. The quenching of the frit, already mentioned in a previous chapter, has an important effect on the milling efficiency. A thoroughly quenched frit will mill much more rapidly than one which contains hard lumps. Such hard lumps are often very troublesome in milling enamels uniformly.

The condition of the slip also affects wet milling; a slip may be too thick or too thin for efficient milling. A very thick slip does not flow enough and retards the balls in their action. It tends to pack and hold the balls together, also acting as a cushion between them. A thin slip runs off the balls and does not, therefore, get between every contact. A slip for best milling should coat the balls uniformly, so that every contact between the balls catches some of the enamel. Such a condition, however, makes the discharge of the mill difficult, since such enamel does not flow well from the mill. A compromise is, therefore, necessary, although many operators reduce the water added when the mill batch is made up and at the end of the run they drain out only that which

will flow. They then add the remainder of the water to the mill and after a few more revolutions the enamel in the mill becomes very fluid and can be readily drained out. Soluble salts (electrolytes) affect the milling by affecting the mobility, yield value, and set of the enamel, the result of which may be understood from the preceding discussion.

MILL ROOM EQUIPMENT

The equipment of the enamel mill room depends upon the requirements of the particular plant. Where the production is small, the operations other than the actual rotation of the mills may be done by labor alone, but, where production is large, extensive conveyor systems and labor-saving equipment are desirable. Economizing on ball mills is not, however, usually considered good practice; it is not generally real economy. Separate ball mills are desirable for widely different types of enamels, the use of the same mill throughout being costly because of labor and material costs involved in cleaning between operations. White cover enamels for sheet iron and cast iron should have separate mills. A special mill should be used for the cobalt ground coat. Color mills should be separated into two groups, those for the dark colors and those for the light colors. If graining enamels are used, a separate mill is often required for them as they are particularly difficult to clean. In addition to these production mills, small laboratory mills should be available for matching colors and for running experimental batches.

Weighing Equipment. Three scales are desirable in most enameling plants; one with a capacity to weigh the bulk materials, such as frit, clay, and water, another to weigh opacifiers and colors, and a third of an accuracy sufficient to weigh electrolytes and special color additions. The bulk scales usually have an accuracy of about one pound, the smaller scale about one-fourth of a pound, and the smallest scale an accuracy of about one-sixteenth of an ounce.

Although the water is sometimes weighed, it is often added to the mill by volume measurement. For this purpose a water meter is sometimes used, but a measuring tank, usually of the overflow type, is much more common.

Miscellaneous Equipment. No discussion will be given here of the different types of conveyors, hoppers, platforms, and layouts for milling, since the diversification is great and requirements are varied.

The screening equipment for the milled enamel is usually a coarse sieve to remove the large particles, such as pieces of balls or "tramp" material in the enamel. In some cases, however, the slip is carefully

screened, one of the more satisfactory methods being by means of vibrating screens or screens of the rotary spray type.

Ball Mills. The general design and construction of ball mills used for vitreous enamels are not essentially different from those used for other purposes. It has already been mentioned that enamels must not be contaminated by iron; therefore ball mills used in the enamel industry must be so lined that no iron will be exposed in the grinding. Two materials are commonly used for lining enamel mills; porcelain bricks and silex blocks. Porcelain bricks, when made of a good tough, well vitrified body, are most popular. These bricks are made in various sizes and shapes to fit the curvature of different mills, but are in general about 2 x 2 x 4 inches in size, being shaped so that they fit together in tight joints. This requires that the sides be beveled so that they will fit flush with each other in the circular construction. They are set in a good grade of portland cement, all joints being kept as thin as possible.

Silex is a natural silica rock which is very finely crystalline. These silex blocks are broken and split out of the massive rock; therefore they have rough surfaces and are very irregular. They, too, are set with portland cement, but it is very difficult to keep the joints thin because of their irregularity and rough surfaces. A silex lining once installed and broken in, however, is a durable lining quite suitable for the milling of enamels. The wide joints are objectionable because of the possibility of contamination from the cement. The rough surface produced by the silex lining is desirable, for it improves the efficiency of grinding. Silex blocks are used more extensively in mills for ground coats than for cover enamels, since there is greater chance for contamination of white enamels from this lining than from porcelain. The contamination from a good grade of porcelain is not very serious as it is very slight and, in addition, this material is white and more fusible in the enamel than the silex. The silex, being a natural rock, often contains dark veins of materials which could cause dark specks in the enamel.

The use of rubber as a lining for enamel mills has not been very popular, although in other industries it has been very successful. It is suitable for wet milling of many materials, but the heat developed in dry milling disintegrates the rubber. Rubber linings should not be used in mills which reach a maximum temperature of over 150° Fahrenheit. A rubber lining is much more suitable for small mills than for large ones, as large balls strike the rubber lining with too great an impact, causing a disintegration of the structure of the rubber. This

TABLE 32
CAPACITIES AND CHARACTERISTICS OF BALL MILLS

MILL	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Inside Diam., Ft.	1	1½	2	2½	3	3½	4	4½	4½	5	5	6	6	6
Inside Length, Ft.	1½	2	3	3½	4	4	5	3½	4½	4	6	5	8	10
Volume, Cu. Ft.	1.6	4	7	10	18	27	44	40	53	58	88	110	186	252
Volume, Gal.	9½	28	40	80	120	200	345	300	400	440	690	840	1390	1755
Enamel Capacity, Lbs.	32	80	104	200	360	544	880	800	1080	1160	1905	2200	3740	5040
Gallons of Slip	6	18	27	50	90	125	215	190	250	275	430	525	870	1100
R. P. M.	42	40	36	30	26	25	23	22	22	21	21	19	19	19
H. P., start	¾	1	1½	3	5	6	7½	8	8¾	9	12	15	22	30
H. P., run	½	¾	1	2	3	4	5	5¼	5¾	6	8	9	15	20
Charge Pebbles, Lbs.	80	200	300	470	850	1300	2200	2000	2750	2900	4600	5500	9300	11,600

objection is largely eliminated in large mills by using thicker linings to take up the impact. Rubber with its high coefficient of friction has the advantage of carrying the charge higher in the mill than other linings. It is claimed that the contamination of white enamels by rubber linings is negligible, but the adoption of this material has been very slow in the enameling industry. Rubber-lined laboratory mills for enamels have proved very satisfactory from the standpoint of efficiency, freedom from contamination, and long life. The doors of enamel mills are often covered with rubber to prevent contamination from the iron of the door-frame.

Both porcelain balls and flint pebbles are used in enamel mills, the latter being usually conceded to have the longer life. As with the siliceous lining, the chances of objectionable contamination with the flint pebbles is greater than with the porcelain balls. The pebbles are usually dark in color and any broken chips getting into the white enamels cause dark specks. They are, however, used considerably for ground coats and colored enamels. If porcelain balls are used, they should be of a good grade of porcelain and well vitrified.

The flint pebbles are obtained along the northern coast of Europe and are sold in the United States as French pebbles No. 1 ($1\frac{1}{2}$ -2") and No. 2 (2-3 $\frac{1}{4}$ ") or Danish pebbles No. 1 (1-1 $\frac{1}{2}$ ") and No. 2 (1 $\frac{1}{2}$ -2"), although larger sizes can be obtained. The standard sizes for porcelain balls are 1", 1 $\frac{1}{4}$ ", 1 $\frac{1}{2}$ ", 2", and 3".

It is good practice, especially when porcelain balls are employed, to use more than one size, because this introduces more points of contact between the balls than can be obtained with a single size. This is unnecessary with the pebbles, for they always vary not only in size, but also in shape.

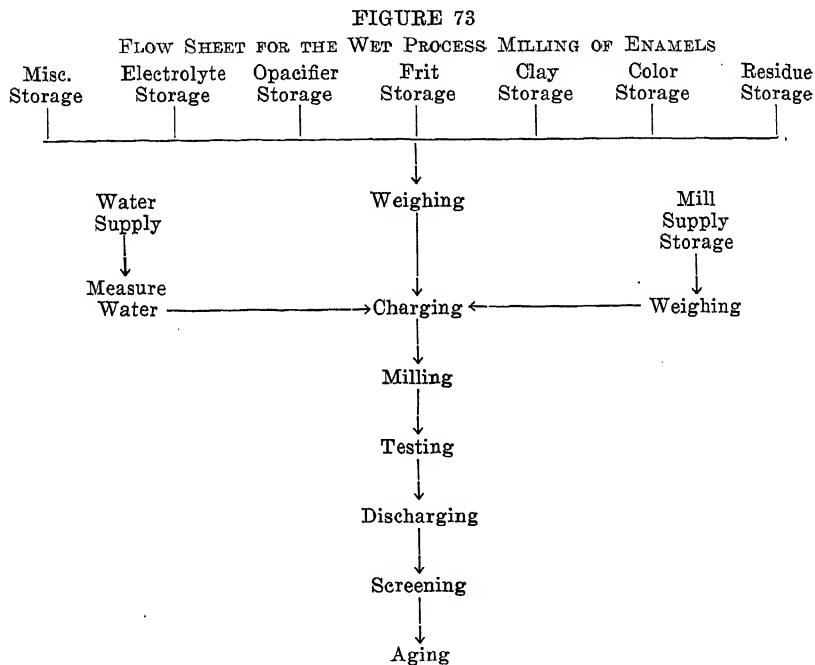
Table 32 gives the capacities and general characteristics of the standard ball mills. It is not possible to give the milling time required for enamels, since this varies over a wide range because of such factors as the size of the mill, the condition of the quenched frit, the hardness of the frit, and the amount of clay. The time required for milling and the optimum number of revolutions have to be determined for each case by actual trials.

MILLING OPERATIONS AND CONTROL

The milling of enamels should follow a definite routine, the specifications should be closely followed, and the records carefully kept. A milling card should be filled out when each batch is made up, the other information being added to the card as it is obtained. The card should

be kept with the batch throughout the whole operation, being hung on the mill during milling and removed only when the batch is removed from the mill. It is convenient to have a perforated identification card, part of which can be torn off after milling, the record going to the files, and the identification card going with the batch to storage.

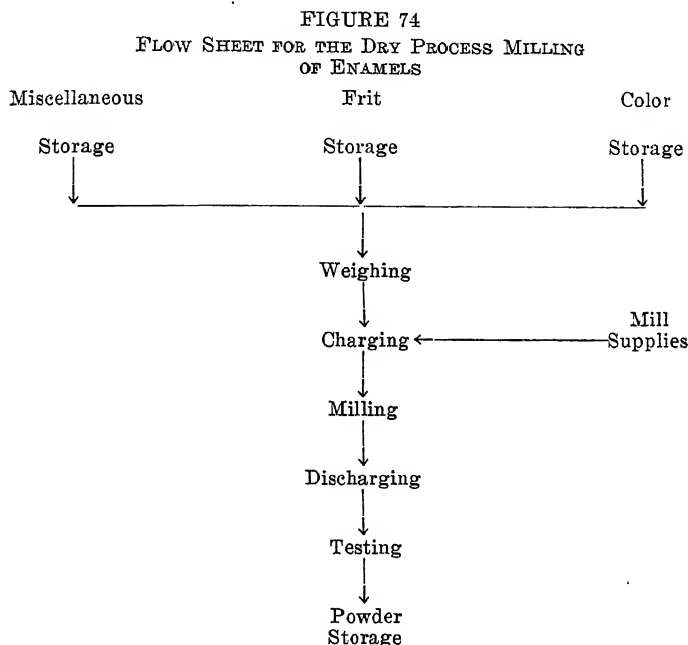
The flow sheets shown in Figures 73 and 74 give the routine operations of milling.



Batch Making. Weighing the batch is the first operation preparatory to milling. The weighing is usually done in a metal hopper with a sliding door at the bottom, the frit being weighed first, followed by the clay and other mill additions. The weighing of the batch seems like a simple operation, but it must be done with great care, for mistakes will have serious consequences. The raw materials must be uniform in properties and chemical composition; the frit should be in the properly quenched and shattered condition, so that it will mill in a reasonable length of time; the clay must be uniform from one batch to another, otherwise the resulting slip will not be uniform; and the opacifiers and the colors must be of known, reliable sources. The elec-

trolytes added for setting up the enamel must be very accurately weighed, and contamination must be avoided by constant observation and care of the materials.

Charging. The charging of the batch into the mill should be preceded by a careful inspection of the mill or definite information as to its condition. If the mill has previously been used for a batch like the one being charged, it is only necessary to be sure that foreign material



or large particles of frit are not present. If a different kind of batch has preceded the one being charged, the mill must be thoroughly cleaned.

The cleaning operation may consist only of washing the mill thoroughly with water or it may involve grinding the mill out with clay, quartz, and water; in other words, the method of cleaning is determined by the condition of the mill. If the latter is contaminated by dark-colored enamel and the present batch is a white cover, the greatest precautions must be taken to clean it thoroughly. In such a case the balls must be emptied out of the mill after it has been ground with a batch of clay, quartz, and water. The inside of the mill must then be flushed out and, if necessary, scrubbed, and the balls thoroughly

cleaned and returned to the mill. If the conditions are not so extreme, the mill may be merely flushed out several times with or without removing the balls.

Dry process mills are cleaned either by milling a small batch of waste enamel, followed by dumping and brushing, or by brushing only. In any case, it is essential that the mill be clean enough not to contaminate the next batch. Experience and judgment are involved here in determining just how thorough the cleaning operation must be. In many enamel shops this uncertainty and labor are avoided by having sufficient mills so that each can be reserved for a particular type of batch. The mills should, however, be periodically cleaned and inspected, even if they are reserved for only one kind of batch.

Before charging the batch to the mill, the charge of balls in the mill should be inspected, so that the correct amount will be used. In a properly organized plant the cleaning and conditioning of the mills is done as part of the regular routine, so that no delay will be encountered when it is desired to prepare a batch of enamel.

The batch is charged into the mill by supporting the hopper over the mill door and opening the slide in the bottom of the hopper. If the colors, opacifiers, or electrolytes are not mixed into the batch during this charging operation, they should be added so that they will be covered by the batch. If these constituents are on top of the batch in the mill, there is danger of their being partly lost, because they may fall into the space between the lining of the mill and the door. Since they are present in only small amounts, such a condition might seriously affect the properties of the enamel.

In wet milling the water is added over the frit. This water must be either weighed or measured by volume, since the amount must be accurately controlled. The volume of the water added can be controlled by the use of either a water meter or a calibrated tank, the latter device usually being considered more dependable.

After charging the material into the mill, the gasket and cover are set in place and securely clamped down; then the air vent is closed, the guard rails put in place, the revolution counter set, and the mill started. All data, including the time, are recorded on the mill card.

Milling. Assuming that the power supply, repairs to the equipment, and the speed of the mills are taken care of, the most important problem in the milling operation itself is to determine when the enamel is properly milled. It is not safe to depend upon the time of milling or even the number of revolutions of the mill for this purpose, because small variations in the conditions often greatly affect the results. An

actual test of the enamel is necessary and is the method used in all well-run plants. This irregularity is probably the reason why continuous mills have been so seldom adopted in the enameling industry. They have found favor in preparing dry process enamels, but have met with little success in wet process milling.

The sample for the *fineness test* is usually taken through a sampling tube in the end of the mill. If such a tube is not used, it is necessary to take a sample through the door. In either case, care must be taken to be sure that a representative sample of the batch is obtained.

The fineness test consists in washing either a known volume or weight of the slip through two sieves. The enamel should all pass the coarser sieve and should leave some residue on the finer sieve. The plant tests vary considerably to suit the particular conditions, the volume of the residue sometimes being measured and, in other cases, the residue is weighed wet or dry. The test used should, in any case, be definitely standardized and carefully run, so that the results will be dependable.

The *cone screen test* is one of the tests which has been popular in enameling shops. These screens are conical in shape, about three inches in diameter at the top, and about five inches long. Usually two screens are used in a test, the measured sample being placed in the coarser screen, in which no residue should be left after water is run through the screen. The enamel which passes the coarser screen is caught on the finer screen and again flushed with water. A definite amount of residue should be retained by the second screen, the amount being measured by a scale on the side of the screen. Such a test is convenient, but it is not as accurate as the standard test, where the residue is caught on a flat screen, dried, and weighed.

The standard method for fineness of wet-milled enamels, which has been adopted by the Enamel Division of The American Ceramic Society is the most desirable method. It is suitable to plant practice and is coming into very common use.

THE STANDARD METHOD FOR FINENESS OF WET-MILLED ENAMELS ADOPTED FEBRUARY 17, 1930.¹

The enamel to be tested should be stirred thoroughly to produce uniformity.

Sample. A sample containing 100 grams of frit should be weighed. This, in grams, corresponds to the total mill charge, including water, for 100 pounds of frit.

Sieves. A No. 40 protection sieve should be placed above the testing sieve. The testing sieve should be either a No. 100, 200, or 325, depending on the fineness

¹ Bul., Amer. Ceram. Soc., 9, 269 (1930).

of the enamel being tested. If, on a trial run, the residue retained on a No. 200 sieve, as testing sieve, is over 25 grams, a No. 100 should be used; if the trial residue on a No. 200 is within the range of 1 to 25 grams, that sieve should be used. The above sieve numbers refer to the United States Standard Sieve Series.

Testing. The weighed or measured sample should be poured onto the upper (protection) screen and carefully washed through the two screens, until no enamel can be detected in the washings. Nothing other than coarse, unground particles should be retained on the protection screen. The lower (test) screen, with its residue, should be thoroughly dried, until the residue thereon easily moves about as a dry powder when the sieve is shaken. The sieve should be tapped gently, until less than 0.1 gram passes through on a minute's tapping.

Weighing. The residue should be transferred to a balance and weighed to the nearest 0.1 gram. The weight thus determined should be taken as the index of fineness of the enamel in terms of the number of the testing screen used.

TABLE 33
PROPERTIES OF TYPICAL ENAMEL SLIPS

TYPE OF ENAMEL	SPECIFIC GRAVITY	FINESS *
Sheet iron ground coats.....	1.55 - 1.75	7 to 20
White sheet iron cover enamels.....	1.80 - 1.90	4 to 7
Colored sheet iron cover enamels.....	1.80 - 1.90	2 to 4
White lead-bearing cast iron enamels.....	2.20 - 2.40	2 to 4
Leadless white cast iron enamels.....	1.80 - 1.90	2 to 6
Colored lead-bearing cast iron enamels....	2.20 - 2.40	1 to 3

* Residue in grams on a No. 200 screen from a 100-gram sample.

Note. Testing sieves of the finer sizes have, in a number of instances, been found in error far more than the commercial tolerances permit. This is especially true of old sieves, because of wear and the corrosive influence of the laboratory atmosphere, but may sometimes be true of new sieves. Reasonable precautions should be taken by the user to assure himself that his sieves are accurate.

It is not possible to recommend a given screen analysis for enamels without the results of trial runs of different screen analyses and the behaviors of the enamels on application, drying, and firing. Enamels differ in their requirements, depending on their compositions and the methods used for application and handling. Typical screen analyses of the different types of wet enamels are, however, shown in Table 33.

If ground coats are milled too fine, there is a tendency to burn off at the edges. They over-fire more readily with the production of delayed fishscale or "shiners." The properties of the slip are affected by grinding too fine, the set-up is greater, more water is required for the same thickness in application, and water streaks may result.

If the ground coat is milled too coarse, a rough surface is produced, copper-heading is aggravated, and the enamel does not stay in suspension well.

If white cover enamels are ground too fine, they tend to tear and the set-up is affected by both the finer particles and the increased solution of the frit in the mill liquor. If the grinding is too coarse, the opacity is reduced and the surface does not fire down smoothly.

Uniform milling greatly aids uniform application, therefore the added effort put into the uniform grinding of the enamel is usually compensated by the gain in application, not to mention the improved quality of the ware. Good milling practice is, in general, uniform practice.

In the milling operation two fineness tests are run, one a short time prior to the discharging, which usually gives the proper fineness, and one just prior to the discharging of the mill. The first test gives information, which by experience enables the operator to estimate approximately how much longer the mill should be run to give the desired condition.

Specific Gravity. The control of the specific gravity of the slip begins with the mill batch. If a constant amount of water is added to each mill batch, the variation in the specific gravity is kept at a minimum. Since the mill lining may absorb more water at some times than others and since the raw materials may carry in small amounts of water, the control of the added water does not always insure a constant specific gravity for a given enamel batch. Variations in the batch will greatly affect the specific gravity of the enamel slip.

To determine the specific gravity of a slip, it is only necessary to weigh a known volume using metric units, and divide the weight in grams by the volume in cubic centimeters. The equipment necessary is determined by the size of the sample used. If equipment is available to weigh accurately to two-tenths of a gram, this, and a hundred cubic centimeter copper tube are all that are necessary. The tube should be about one inch in diameter and closed at one end. It should be fitted with a flange, so that it will stand vertically, and should be calibrated to hold exactly one hundred grams of water at seventy degrees Fahrenheit.

To make a test, the dry empty tube is first weighed and then filled with the enamel slip to be tested. It is then re-weighed and the weight of the empty tube subtracted from the weight of the tube filled with enamel. This gives the weight of the one hundred cubic centimeters of enamel slip. This weight in grams divided by the volume in cubic centimeters is the specific gravity of the slip. The weighing and volume measurements should be done with sufficient accuracy to give the specific gravity to the second decimal place.

It is not possible to recommend a certain specific gravity for enamels in general, since the specific gravities of the frits vary and the requirements are not the same for different purposes. Table 33 shows the approximate specific gravities used for the different types of enamels.

If the enamel slip has too high a specific gravity, the proper amount of water to be added can be calculated as follows:

$$W = V \times \frac{S_1 - S_2}{S_2 - 1}$$

where V = volume of the slip in gallons,

S_1 = original specific gravity,

S_2 = desired specific gravity,

W = gallons of water to be added.

The chart in Table 34 shows the amount of water in pounds necessary to be added to ten gallons of slip of a given specific gravity to bring it to the desired specific gravity. To change pounds of water to gallons, divide by 8.3454. A similar chart can be conveniently constructed to cover the range of variations ordinarily encountered with a particular enamel.

If the specific gravity of the slip is less than that desired, it must either be allowed to dry out or be blended with a slip of high specific gravity. The former method is inconvenient and not usually considered good practice; it will either require heating of the slip or standing for a long time. Such treatments change the properties of the slip.

To calculate the proportions of two slips, (one with too low a specific gravity and one with too high a specific gravity), necessary to obtain a given desired specific gravity, the following formulæ can be used:

For a given amount of the slip of the lower specific gravity,

$$B = \frac{H - D}{D - L} \times A$$

where H = specific gravity of slip of high specific gravity,

D = specific gravity of slip of desired specific gravity,

L = specific gravity of slip of low specific gravity,

A = gallons of slip of low specific gravity,

B = gallons of slip of high specific gravity.

For a given amount of slip of the higher specific gravity, the following formula is used,

$$A = \frac{D - L}{H - D} \times B$$

where the letters represent the same magnitudes as in the preceding formula.

To change the pounds of either slip to gallons, divide by the specific gravity of the slip and by the factor 8.3454.

Discharging. A mill should never be discharged until the control tests show that the enamel has been properly ground. The enamel is then discharged and put into storage, where, in the wet process, it is aged from twenty-four to forty-eight hours.

The method used for discharging the mill depends upon whether the enamel is milled wet or dry, the ease with which it flows out of the mill, and the equipment available. Dry process enamels are practically always discharged by replacing the mill door by a grating, just coarse enough to retain the balls, and rotating the mill. The latter is enclosed by an apron, which catches the powder as it is thrown out of the mill. The powder falls into a hopper below the mill, from which it is transferred to the storage cans. The enamel in these cans is usually tested by firing small samples, which will show the existence of any defects, such as dirt in the enamel, a lack of gloss, or an off-colored product. If continuous mills are used, the powder is continuously discharged and periodically tested for fineness and firing properties. Dry process enamels are not usually screened, although they may be passed over a coarse sieve to eliminate any foreign materials or particles chipped off the balls or lining.

Wet process enamels may be discharged from the mills, either through a valve in the door or through a mushroom valve placed in the side of the mill. The mills are turned to a position with the valve down for this purpose, the sampling tube is opened to allow air to enter the mill over the enamel, or air is forced into the mill under about six pounds pressure to increase the rate of flow. High pressures should not be used for this purpose, because the ordinary mill is not constructed to withstand much pressure. Small mills may be emptied by the use of a grating in place of the door, the mill being slowly turned until the enamel pours out.

The ease with which enamel slips run out of the mills varies with the consistency of the enamel. A slip which is very thick will run out only very slowly and incompletely. Such slips because of their con-

TABLE 34

CHART FOR CHANGING SPECIFIC GRAVITY

GIVEN IN POUNDS OF WATER PER TEN GALLONS OF SLIP *

ORIGINAL SPECIFIC GRAVITY

	1.625	1.630	1.635	1.640	1.645	1.650	1.655	1.660	1.665	1.670	1.675	1.680	1.685	1.690	1.695	1.700	1.705	1.710	1.715	1.720	1.725	1.730
1.625		0.67	1.33	2.00	2.67	3.33	4.00	4.67	5.33	6.00	6.67	7.33	8.00	8.67	9.33	10.0	10.7	11.3	12.0	12.7	13.3	14.0
1.630	0.66		0.66	1.32	1.98	2.64	3.31	3.96	4.63	5.30	5.95	6.62	7.27	7.95	8.60	9.26	9.92	10.6	11.2	11.9	12.6	13.2
1.635	1.31	0.66		0.66	1.31	1.97	2.62	3.28	3.94	4.60	5.25	5.91	6.56	7.22	7.88	8.54	9.20	9.85	10.5	11.1	11.8	12.4
1.640	1.95	1.30	0.65		0.65	1.30	1.95	2.60	3.26	3.91	4.56	5.21	5.86	6.51	7.16	7.81	8.46	9.12	9.77	10.4	11.1	11.7
1.645	2.58	1.94	1.29	0.65		0.65	1.29	1.94	2.58	3.23	3.88	4.52	5.17	5.82	6.46	7.11	7.76	8.40	9.05	9.70	10.3	11.0
1.650	3.20	2.56	1.92	1.28	0.64		0.64	1.28	1.92	2.56	3.20	3.85	4.48	5.13	5.77	6.41	7.06	7.69	8.34	8.98	9.62	10.3
1.655	3.82	3.18	2.54	1.91	1.27	0.64		0.64	1.27	1.91	2.54	3.18	3.82	4.45	5.09	5.74	6.36	7.00	7.64	8.27	8.91	9.55
1.660	4.42	3.79	3.16	2.53	1.90	1.26	0.63		0.63	1.26	1.90	2.53	3.16	3.79	4.42	5.06	5.69	6.32	6.95	7.59	8.22	8.85
1.665	5.02	4.39	3.76	3.14	2.51	1.88	1.25	0.63		0.63	1.25	1.88	2.51	3.14	3.76	4.39	5.02	5.65	6.27	6.90	7.53	8.16
1.670	5.60	4.98	4.36	3.74	3.11	2.49	1.87	1.24	0.62		0.62	1.24	1.87	2.49	3.11	3.74	4.36	4.98	5.60	6.23	6.85	7.47
1.675	6.18	5.56	4.94	4.33	3.71	3.09	2.47	1.85	1.24	0.62		0.62	1.24	1.85	2.47	3.09	3.71	4.33	4.94	5.56	6.18	6.80
1.680	6.75	6.15	5.52	4.91	4.29	3.68	3.07	2.45	1.84	1.23	0.61		0.61	1.23	1.84	2.45	3.07	3.68	4.29	4.91	5.52	6.15
1.685	7.31	6.70	6.09	5.48	4.87	4.26	3.65	3.04	2.44	1.83	1.22	0.61		0.61	1.22	1.83	2.44	3.04	3.65	4.26	4.87	5.48
1.690	7.86	7.26	6.65	6.05	5.44	4.84	4.23	3.63	3.02	2.42	1.81	1.21	0.60		0.60	1.21	1.81	2.42	3.02	3.63	4.23	4.84
1.695	8.40	7.80	7.20	6.60	6.00	5.40	4.80	4.20	3.60	3.00	2.40	1.80	1.20	0.60		0.60	1.20	1.80	2.40	3.00	3.60	4.20
1.700	8.94	8.34	7.76	7.15	6.56	5.96	5.36	4.77	4.17	3.58	2.98	2.38	1.79	1.19	0.60		0.60	1.19	1.79	2.38	2.98	3.58
1.705	9.46	8.86	8.28	7.69	7.10	6.51	5.92	5.33	4.73	4.14	3.55	2.96	2.38	1.77	1.18	0.59		0.59	1.18	1.77	2.38	2.96
1.710	10.0	9.40	8.81	8.22	7.64	7.05	6.46	5.88	5.29	4.70	4.11	3.53	2.94	2.35	1.76	1.17	0.59		0.59	1.17	1.76	2.35
1.715	10.5	9.91	9.33	8.75	8.16	7.58	7.00	6.42	5.83	5.25	4.67	4.08	3.50	2.92	2.33	1.75	1.17	0.58		0.58	1.17	1.75
1.720	11.0	10.4	9.85	9.26	8.68	8.11	7.52	6.95	6.37	5.79	5.21	4.64	4.06	3.48	2.90	2.32	1.74	1.16	0.58		0.58	1.16
1.725	11.5	10.9	10.3	9.77	9.20	8.63	8.05	7.48	6.91	6.33	5.75	5.18	4.60	4.03	3.45	2.88	2.30	1.73	1.15	0.57		0.57
1.730	12.0	11.4	10.8	10.3	9.71	9.14	8.57	8.00	7.43	6.86	6.29	5.71	5.14	4.57	4.00	3.43	2.86	2.29	1.71	1.14	0.57	

* W. G. Martin, W. W. Higgins and G. L. Bryant, A. O. Smith Corp.

SPECIFIC GRAVITY DESIRED

sistency must often be milled with insufficient water and partially drained out of the mill in this thick condition. The remainder of the water is then added to the enamel left in the mill. This water gives a very fluid slip, which can be readily drained out. If the mill is used repeatedly for the same enamel batch, a small amount of residue left in the mill is not objectionable, for it is not lost. A large amount, however, reduces the capacity of the mill and may lead to an excessive amount of fines in the slip.

Mills are usually mounted well above the floor to facilitate draining, since it is usually necessary to place a container under the mill large enough to hold an entire batch. In some cases the drained enamel is pumped directly from the mill to the screens or to storage. A diaphragm slip pump is most satisfactory for pumping enamels. Some pumps agitate the enamel excessively, causing it to heat and thereby influencing its set.

In any case, one should avoid contamination of the product by dirt or other foreign materials when discharging enamels from the mill. It is good practice in this regard to wash the outside of the mills and keep the mill room generally clean. Smoke and dust in the air of a mill room should be avoided.

Screening. Enamel slips are preferably screened to eliminate any large particles which may interfere with the spraying or cause lumps in the enamel coating. The flat reciprocating screen has been used extensively for this purpose, but the rotary type of screen has a much greater production and is being more generally adopted. The enamel slip is fed into a funnel at the upper end of a shaft, down which it runs to the rapidly revolving spray head. The centrifugal force of this spray head throws the slip in a fine spray through the screen surface. The portion of the slip which does not pass the screen flows down into the residue tank, where it is picked up by the revolving cone and again thrown into the screen.

Such a screen will handle several hundred gallons of slip per hour, an eighty-mesh sieve being used for cover enamels and a sixty-mesh sieve for ground coats.

Aging. The aging of enamels is usually desirable, although certain types, such as some acid-resisting enamels, do not work as well when aged. However, enamels which are to be dipped or slushed onto the ware are, in general, better if aged for one to two days.

When enamels are discharged from the mill they are usually warm from the friction in the mill and have different properties than when they cool. The temperature of enamels not only has an important

influence upon the properties at that temperature, but it affects the final condition of the enamel. Enamels should, therefore, be aged at temperatures close to those at which the enamel is to be applied. In the aging of enamel slips an equilibrium is set up between the clay, the frit, and the solution. If this equilibrium is maintained, the properties of the slip remain constant, but a slip which is agitated or subjected to different temperatures will change in properties because of variations in this equilibrium. At higher temperatures more solution takes place, at lower temperatures it is reduced. If a slip is, therefore, subjected to varying temperatures, it will tend to change in properties and control will be very difficult. In some cases the ball mills are kept cool during milling, so that the slip will not be exposed to elevated temperatures, which change its properties. A slip which is undergoing changes is difficult to handle in application, therefore aging is essential to good practice. Most enamellers are familiar with the difficulties encountered by the use of the cold ground coat slip on a Monday morning after a shut down.

Enamels vary in their abilities to reach an equilibrium on aging. Some enamels attain it in a comparatively short time, while others continue to change over a long period. Agitation accelerates the rate of aging. If the frits used in the enamel are fairly soluble in the mill liquor, aging may be a detriment to them, since their natural equilibrium will then be a condition in which the enamel cannot be used. Such slips must, therefore, be used before they have aged very long. The release of air bubbles which have been trapped in the slip during the milling operation is another advantage of aging.

A uniform slip is usually an aged slip and practice has shown that the slip which will withstand aging is usually the easiest to handle. A slip which cannot be aged may be a constant source of trouble, because difficulty is usually encountered in getting and holding it in the proper condition for use. The discussion of the function of electrolytes, the effects of soluble salts, and the properties of slips, Chapter 10, is of interest in the consideration of aging.

Reclaiming Enamel. In practically all enameling shops the reclaiming of waste enamel is an important problem. In the dry process shop this waste is in the form of floor enamel, *i.e.*, that which is caught in the tray on the floor under the dusting-on equipment. This floor enamel contains particles of scale and dirt, which make it unfit for use without reconditioning.

Floor enamel is reclaimed by first screening out as much as possible of the foreign material and, in some instances, passing it over a

magnetic separator. Enamel treated in this way may in some shops be used for ware not requiring as high a quality as the first-grade product. If the enamel cannot be used after this preliminary treatment, it is usually incorporated in the raw batch and resmelted. Smelting brings about a further purification and dilutes the foreign materials. The difficulties of reclaiming floor enamels depend to a great extent on how well they are protected from undue contamination. It is usually easier to eliminate sources of contamination than to correct the trouble.

In wet process enameling the spray booth residue constitutes the main source of scrap enamels. This enamel is often contaminated by sand from castings, dirt carried in by the ware, dust collecting from the air, and other miscellaneous articles, which may fall into it. Here it is desirable to eliminate as much chance for contamination as possible.

The spray booth scrap is reclaimed in a number of different ways. If the scrap is dry, it is usually screened through a No. 20 sieve, but, if it is wet, it may be stirred into an excess of water, skimmed to remove floating materials and then screened.

There are two ways of preparing the residue for re-use; blunging it with additional clay and a small addition of opacifier, or remilling it with similar additions, or as an addition to the regular mill batch. The first method of blunging is not common, but it has the advantage of not reducing the fineness of the frit. When reconditioned, the resulting slip is generally used for the first cover coat enamel only.

The method of remilling the screened residue is most common, the milling being continued only long enough to give thorough mixing. Such mill additions as one per cent of clay and one per cent of opacifier are generally used if the enamel is to be used as the first white coat. In many plants it is convenient to use this reclaimed enamel in the making of grays or other dark-colored enamels by the addition of colors and remilling. The principal objection to remilling the scrap is the danger of grinding it too fine.

MILL ADDITIONS

Although mill additions make up only a minor part of enamel compositions, they have an important effect on the properties both before and after firing. In some cases more than one frit is used, but this is usually unnecessary. Sheet iron ground coats are often made in two frits, one hard and one soft, which makes it possible to vary the hardness of the enamel by varying the proportions of the two frits. It is true that with some compositions, better and more dependable

results can be obtained with two ground coat frits blended together than with one frit of the blended composition.

Mill additions for enamels can be classified into four groups in addition to the water and the frit. These groups are: floating agents, opacifiers, colors, and electrolytes.

The water for mill additions should be the same from day to day, as the mineral content of the water influences the properties of the slip. Mill waters must be free from mud or other suspended materials, which tend to form dark specks or blisters in the enamel. It is necessary when using roily waters to filter them through sand or other filtering material. Since natural waters often contain appreciable amounts of dissolved salts, such as calcium and magnesium sulphates and carbonates, their mineral content is of considerable importance. In some waters the alkali runs high and in others iron salts may be objectionable. The finely divided animal or vegetable matter is not usually detrimental, unless it is especially abundant.

Floating Agents. Floating agents are materials, such as clay and gums, which suspend the frit particles in the slip. Clay is the most common floating agent, but the selection of the clay is an important consideration. There are no simple tests for the selection of enameling clays, therefore an actual trial in the enamel is usually made. Clays for enamel mill batches should be fine grained and highly plastic, but they should not contain appreciable amounts of impurities, such as mica and organic materials. Good enameling clays, when fired alone, are cream-colored and contain no dark specks. They are refractory and their chemical compositions approximate kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The properties and chemical compositions of six typical enamel clays are shown in Table 35.

It is evident on studying this table that a determination of the physical, drying, and firing properties and the chemical compositions do not enable one to select a good enamel clay. The work by Rice and Poste² and also that of Boeker,³ from which some of these figures were taken, further substantiate this conclusion.

Enamel clays are usually of the plastic ball or fire clay type. They must be uniform from shipment to shipment and must be fairly free from iron and coarse grained impurities. In some enameling shops the clay is suspended in water and screened through a No. 200 mesh sieve to eliminate foreign materials. This is often desirable, since it is an inexpensive operation, which may eliminate frequent specks or fish-

² B. A. Rice and E. P. Poste, *Bul. Am. Ceram. Soc.*, 9, 230 (1926).

³ V. W. Boeker, *J. Am. Ceram. Soc.*, 9, 399-411 (1926).

scale in enamels. It is particularly recommended for white or light-colored enamels of high quality or when large units of ware are being made.

There are many good enamel clays of both domestic and foreign origin on the market. Some of these clays are carefully refined before marketing and some are ground to a powder and thoroughly mixed to improve the uniformity.

Gums are used as floating agents in some types of enamels, particularly those used for sign work or those designed particularly for resistance to acid solutions. Gum arabic and gum tragacanth are most common, these being made up with water to a thin jelly and added as such to the enamels. These gums are objectionable in enamels which are stored for a long time, because nodules or lumps slowly form in the

TABLE 35
PROPERTIES OF ENAMEL CLAYS

Clay	Drying Shrinkage	Firing Shrinkage	Color Fired	Relative Viscosity	pH Value	Fineness. Per Cent on 300 Mesh	SiO ₂	Al ₂ O ₃ Fe ₂ O ₃	CaO	MgO	Loss on Ignition	Alkalies by Difference
Amer. A	33.2	13.2	pink	1.54	6.0	0.35
Amer. B	23.8	6.2	white	4.4	1.5	53.8	31.9	0.2	0.12	11.3	0.14
Amer. C	39.5	14.3	cream	1.86	4.0	1.42	47.1	35.0	0.33	0.46	14.5	2.7
Amer. D	35.1	8.8	buff	1.89	4.0	8.6	57.7	29.4	0.21	0.29	10.1	2.3
German	30.7	9.9	buff	2.34	6.6	1.1
English	32.8	29.6	white	1.45	6.4	1.45	57.7	31.1	0.44	0.16	9.1	1.6

slip. A trace of carboric acid added to slips prevents bacterial action on the gums.

Gums are frequently used to control the hardness of the enamel after it has been dried on the ware. Such control is important to the brushing operation, since enamel which does not dry hard enough becomes damaged, and enamel which dries too hard is difficult to brush off. The efficiency of the brushing operation is dependent on having the enamel of proper dry hardness. Gums in acid-resisting enamels are advantageous, because they do not lower the acid resistance, as clay does. The set-up of acid-resisting enamels is often difficult and in some cases the use of gums shows an advantage over clay for this reason. Ammonium alginate, which is closely related to the gums in its use for suspending enamels, is used in extremely small amounts and for some enamels seems to be superior to other materials. Bentonite is probably more closely related to the clays than the gums, since it is a highly

colloidal clay. It is not generally used alone, but in conjunction with clay. Because of its colloidal behavior smaller amounts of clay can be used. Sodium aluminate has also found considerable favor in suspending enamels.

Opacifiers. Both tin oxide and zirconium oxide are commonly used as opacifiers in the mill addition of white enamels, and in isolated cases small amounts of sodium antimonate and titanium oxide are used. A complete discussion of the theory of opacity is given in Chapter 3. Opacifiers added to the mill have less chance to dissolve in the enamel than those added in the raw batch before smelting. This aids in the conservation of the opacifier, but must not be carried to excess or a mottled effect will result. It is almost universal practice in wet process enamels to use a frit having some opacity, and through the mill addition bring the enamel to good quality. Zirconium oxide is seldom, if ever, used in the raw batch, and tin oxide is used in the raw batch only for dry process enamels or those of a special type.

Tin oxide used as an opacifier should be of the best grade available. It should be white to creamy white in color with very few dark specks, when observed under a microscope. It should not contain stannous oxide, which is black, nor metallic tin. A simple test will show the presence of these impurities, thus: place a small amount (about 25 grams) of the tin oxide to be tested in a glass beaker and fill the beaker with water. Stir thoroughly and note any floating impurities; then pour off the suspended tin oxide, being careful not to disturb the residue. Refill the beaker with water and repeat the process several times; then examine the residue for black particles. Metallic tin and stannous oxide have a higher specific gravity than the stannic oxide, therefore they will tend to settle more rapidly than the stannic oxide. No dark particles should be found in the bottom of the beaker, when a good grade of tin oxide is tested.

Commercial tin oxides vary considerably in their opacifying properties in enamels, the best test being a trial with the enamel used. The opacifying properties of tin oxide are as much dependent on its physical properties as on its purity.

Zirconium oxide is usually very free from harmful impurities, but it does contain considerable foreign material, which cannot be eliminated in its preparation. Zirconium oxide of a good grade should not show dark specks when examined under a microscope and should contain a high percentage of zirconium oxide. Its opacifying power is best checked by a trial in a batch of enamel, for it is more satisfactory in some enamels than in others. It is always added at the mill, usually

in slightly greater amounts than is required of tin oxide. Since it produces a whiter color than tin oxide, a tin color zirconium oxide is now available in which a stain is used to give the cream color which is sometimes desired.

Colors. The color materials added at the mill represent a wide range of possibilities, almost any color being available. Dark blues and blacks are, however, usually made from colored frits.

The frits used for making colored enamels may be summarized as follows:

1. Colored frits,
2. White opaque frits,
3. Transparent or nearly transparent frits.

In general, it can be stated that pure dark colors are made by the use of colored frits, pastel tints by the use of white opaque frits, and opaque colors by semi-transparent frits. In wet process enameling the use of opaque frits is not uncommon, but in the dry process such frits cause a mottling effect, which is not generally desired.

The making and particularly the matching of colored enamels requires experience, since there are no general rules which can be followed. Such variables as the composition of the frit, the compositions and combinations of the color materials added, the milling, other mill additions, and the firing make almost every color an individual problem.

In general, however, the addition of opacifiers or the use of white frits tends to induce the development of pastel tints. The opacifiers contribute a white color, which dilutes the other colors and contributes an opaque body to the enamel. Blacks often react with the other color oxides, but the shade is darker with increased amounts of black oxide.

The blending of colors in enamels is often quite disappointing, as chemical reactions are likely to interfere with scientific color blending. Red and yellow produce orange in most cases, but, until experience has been gained, such blending is guess work and must be supplemented by trial and error experiments. After gaining experience, however, it is possible to blend many colors and match almost any desired color, shade, or tint.

The composition of the frit further affects the color by its chemical reaction with the coloring materials. For example, a lead-bearing enamel may produce a dirty brown or green with red or yellow color oxides of the selenium type. Antimony compounds in the presence of

TABLE 36
THE COMPOSITIONS OF TYPICAL STAINS, AND THE AMOUNTS USED IN
ENAMEL MILL BATCHES

COLOR	BLUE			GREEN			BLUE-GREEN			GRAY	YELLOW			BROWN			RED		
	D	M	L	D	M	L	D	M	L		2-4	5-10	12	D	M	L	D	M	L
	2-3	2-3	2-3	2-5	2-5	1-5	2-4	2-4	2-4		1	5-10	5-10	5-10	5-10	5-10	1-4	1-4	1-4
AMOUNT USED (%)	12	8	8	12	5	8	6	6	6	5	12	1	8	1	8	1	(5 min. 500 G)		
Calcined at cone	55.4	51.6	54.8	33.0	33.0	56.3	8.0	47.5
Aluminum oxide.....	32.0	23.1	8.0	49.1
Antimony oxide.....	57.7	72.0
Cadmium oxide.....
Cadmium sulphide.....
Calcium carbonate.....	3.5	3.5	20.0
Calcium chloride.....	12.0
Chromic oxide.....	66.2	50.0	15.8	49.0
Cobalto-cobaltic oxide.....	44.6	55.5	35.5	6.2	15.8
Cobaltous chromate.....	28.2	7.4	12.0
Fluorspar.....
Iron oxide (red).....	15.8	18.5	15.1
Lead oxide (red).....	44.0
Manganese oxide.....	52.6	51.0
Nickelic oxide.....	33.8
Potassium dichromate.....	7.0	36.0	11.5	31.5	37.5	34.0	30.2
Potassium nitrate.....	1.0
Selenium (black).....	20.0
Silica.....	35.0
Sulphur.....
Tin oxide.....
White lead.....	3.5
Zinc oxide.....	20.2	37.8

Ref. Harrison and Hartsborn, J. Am. Ceram. Soc., 10, 747 (1927).

lead form yellow lead antimonate, and chromium may form lead chromate. Manganese, nickel, and iron are sensitive to the enamel composition, both alone and in the presence of each other. It is because of these facts that black is such a difficult color to produce uniformly.

The degree of milling has an important influence on color, the color being more intense as the fineness increases. This fact requires very careful milling of color enamels, otherwise a considerable variation from one batch to another will exist.

Some colors such as reds and blacks are very sensitive to the furnace atmosphere and most colors are affected by the time and temperature of firing.

Thickness of application is a factor of particular importance in transparent colored enamels, and often a source of annoyance.

Pure color oxides, such as cobalt, chromium, nickel, and iron oxides are not generally added as a mill addition, because they are not then easily distributed through the enamel in a pleasing uniform manner. They require excessive grinding and do not give as strong a color, for the actual amount added, as they do, if they are used as stains. These stains, or "color oxides" as they are sometimes called, are calcines of mixtures of the pure color oxides plus fluxes or frits. They are carefully prepared to insure uniformity and are milled very fine.

Although it is possible for the enameler to make his own stains, it is much more satisfactory for him to purchase them from someone who makes a specialty of their manufacture. The control is difficult, when conditions are at their best, therefore, unless these materials are used in very large quantities, the enameler does not make them.

Table 36 gives the compositions of typical color stains and the amounts used as mill additions to produce different colors. In using these stains it should be remembered that the composition of the enamel often affects the color.

Table 24 gives the compositions of dark blue and black frits, such colors being much more successful when smelted into the enamel.

The enameler should be familiar with the principles of color, as outlined in Chapter 3.

Electrolytes. Electrolytes are soluble compounds added to the mill batch to control the properties of the slip. Since enamel slips contain colloidal materials, such as clay, small frit particles, and the other fine-grained mill additions, they are quite sensitive to these electrolytes. Their action is described in Chapter 10.

They include such materials as borax, magnesium sulphate, sodium carbonate, and many other similar salts, which ionize, often forming buffer solutions.

The electrolytes may be added either when the mill batch is made, toward the end of the milling operation, or after the slip has been removed from the mill. If added early in the milling, the slip does not drain as easily from the mill, but the fact that they are then thoroughly incorporated in the slip makes this practice the most common. At least part of the electrolytes are usually added when the mill batch is made.

CHAPTER 10

Application and Control

An enamel slip is a complex system consisting of a suspension of several solid phases in one liquid phase. The solid phases vary in particle size from colloids to forty-mesh material, including constituents such as frits, clay, opacifiers, and color oxides. The liquid phase, usually a water solution, may contain gum tragacanth, ammonium alginate, dextrin, or syrup and also electrolytes in the form of soluble salts, acids, or alkalies. The composition and properties of the solution affect the peptization of the colloidal solids, which, in turn, affect the suspension of all of the solid phases present.

PHYSICAL AND CHEMICAL CONSIDERATIONS

Although a slip has some of the properties of a liquid, it also has some of the properties of a solid and, therefore, it does not follow the simple laws of either. Its physical properties are subject to such phenomena as adsorption, peptization, common ion effect, chemical reaction, temperature changes, and pressure changes.

It is probable that adsorption plays an important rôle in these slips, the clay and frit actually adsorbing salts from the liquid phase. The effect on color, dispersion of the solids, interfacial tension, and particle adherence are undoubtedly related to this phenomenon.

The flocculation and deflocculation (peptization) of the colloids by soluble salts, acids, or alkalies control the suspension, not only of the colloidal material, but also the non-colloidal particles. The yield value and the mobility are affected by the peptization of the colloids.

The common ion effect controls the amount of ionization of some compounds and to a certain extent the solubility. The buffer action of compounds, such as borax, controls this phenomenon, keeping the hydrogen ion concentration the same, even though appreciable changes are made in the system. Borax dissolves in the mill liquor, but it ionizes only to a certain extent, depending on the Na^+ and BO_3^{---} ions present in the solution. If these ions are removed, the borax ionizes to replace them and, if more are added, the ions combine to form borax in solution. Since the peptization of the solution is dependent on the free ions, borax acts as a buffer, which within certain limits keeps the degree of peptization constant. Since Na^+ in water forms a strong base and the BO_3^{---} a weak acid, the resulting solution is alkaline and high in

OH⁻ ions and, therefore, the pH value of the solution is also controlled by this buffer action. Although it is true that enamel slips can undergo great changes in properties without undergoing any change in pH value, it is also true that certain physical properties may be greatly affected by the hydrogen ion concentration.

These variable conditions can be controlled to a certain degree, but the usual method is rather to control the properties of the slip itself, as will be explained later in this chapter. Different enamels set up such different conditions and behave in such characteristic manners as to make the prediction of the properties of a slip uncertain.

Suspending Agents. The properties of the clay used for suspending an enamel frit are an important consideration, but the only reliable method of determining the suitability of a clay for an enamel slip is by an actual trial in such a slip. An enamel clay should be plastic, since the plastic clays have a much greater suspending power than those of low plasticity. It is usually desirable to add as little clay as will serve the purpose, because clay increases the refractoriness of the enamels and reduces the resistance to solution by acids. The special clays such as bentonite, which have very high plasticity, are sometimes used, but they have not met with very great favor. An enamel clay should be fairly pure and should not contain much free organic material, iron compounds, or soluble salts. It should burn to a light color without dark specks. There are many enamel clays on the market, but the choice depends largely on a trial test with the enamel to be used. Besides the property of suspending the enamel, the clay must give the dried slip an adherence to the ware and a hardness which permits handling. Some clays fulfilling the above properties are, however, not suitable for enamels because of the tendency to cause the enamel to pinhole and blister on firing. A large excess of clay causes cracking of the enamel in drying, and too little clay results in a dusty coating, which will not withstand the ordinary abuse of handling the ware.

The use of gums and other organic materials to suspend enamel frits is usually limited to special types. In the sign industry, gum arabic is common, although even here it is not universally used. It aids in strengthening the dry enamel, so that stencil brushing does not damage the coating.

When gums are used, they are ordinarily boiled with water to make a gel, and this gel is added to the enamel batch. The addition of the dry gum would result in too slow absorption by the slip and possibly result in some of the gum never being absorbed at all.

Such materials as clay, gum arabic, dextrin, milk, ammonium alginate, and syrup act physically to keep the frit particles in suspension. They tend to make up a skeleton, in which the frit is enmeshed.

Another group of materials, which has more of a chemical action, is the electrolytes which either alone or more commonly with clay bring about the suspension of the enamel frit. Some of these electrolytes such as the salts of magnesium, calcium, and barium, tend to form gelatinous compounds which assist by means of their physical characteristics. Other salts such as borax form buffer solutions which, by this means, control the alkalinity of the solution, thus influencing the suspension because of their peptizing action on the colloidal material present. Acids act directly on the frit, causing it to stay in suspension fairly well, even in the absence of clay.

Solubilities of Frits. Different frit compositions behave differently with respect to the effect of their treatment, so that no set rules can be laid down for the control of enamel slips. The variations in the solubilities of the frits are the chief cause of these differences, although the other factors already mentioned have their own specific influences. Some enamel slips improve with aging, while others become continually worse.

While Staley¹ and Poste² pointed out that the work of Mayer³ and Ashley⁴ on glaze suspensions was also applicable to enamel slips, more recent work by Cook,⁵ Danielson,⁶ and Cooke⁷ has added a great deal to our knowledge of this subject. Table 37 shows the solubilities of ten typical sheet iron enamels, as reported by Danielson. In this study, he used ten pounds of frit milled to 150 mesh (2.4 gram residue) with 5 per cent clay, 6 per cent tin oxide, 0.25 per cent magnesium carbonate, and 42 per cent of water for two and one-half hours. The slip was then aged for twenty-four hours and fifty cubic centimeters of the mill liquor was taken and analyzed.

The results show that an enamel slip contains an appreciable amount of soluble materials, among which sodium oxide and boric

¹H. F. Staley, *Materials and Methods Used in the Manufacture of Cast Iron Wares*. Bureau of Standards, Tech. Paper, No. 142, p. 75.

²E. P. Poste, *Analysis of Suspensions of Enamels*, J. Am. Ceram. Soc., 9, 232 (1925).

³Arthur Mayer, *A Peculiar Property of Some Glazes*, Trans. Am. Ceram. Soc., 11, 369 (1909).

⁴H. C. Ashley, *Control of Colloidal Matter in Clay*, Bur. of Standards, Tech. Paper, No. 23, p. 102.

⁵H. L. Cook, *Some Observations on the Aging of Enamels*, J. Am. Ceram. Soc., 10, 334 (1927), and *Note on the Solubility of Enamel Frit in Mill Water*, J. Am. Ceram. Soc., 10, 339 (1927).

⁶R. R. Danielson, *Effects of Soluble Salts on the Properties of Enamels*, J. Am. Ceram. Soc., 12, 538 (1929).

⁷R. D. Cooke, *A Study of Soluble Salts in Enamels*, J. Am. Ceram. Soc., 13, 658 (1930).

oxide are the most conspicuous. Since these two oxides do not exist together in solution without combining to form borax, it is evident that borax is actually present. A comparison of the enamel compositions and the analyses of the mill liquors indicates that the solubility increases with an increase of boric oxide and also with a substitution

TABLE 37
COMPOSITION AND SOLUBILITY OF SOME TYPICAL SHEET IRON ENAMELS
MELTED COMPOSITION

<i>Enamel</i>	<i>Feldspar</i>	<i>Flint</i>	<i>Boric Oxide</i>	<i>Sodium Oxide</i>	<i>Cryolite</i>	<i>Fluorspar</i>	<i>Sodium Anti-monate</i>	<i>Zinc Oxide</i>
1	30	20	11.7	8.3	15.0	7	8	0.0
2	30	20	11.7	8.3	12.5	7	8	2.5
3	30	20	8.7	8.3	12.5	7	8	5.5
4	20	30	8.7	8.3	12.5	7	8	5.5
5	30	23	8.7	8.3	12.5	4	8	5.5
6	23	30	8.7	8.3	12.5	4	8	5.5
7	30	21	8.7	10.3	12.5	4	8	5.5
8	21	30	8.7	10.3	12.5	4	8	5.5
9	27	21	8.7	10.3	12.5	4	8	8.5
10	21	27	8.7	10.3	12.5	4	8	8.5

SOLUBILITY (10 CC. MILL LIQUOR CONTAINED IN GRAMS)

<i>Enamel</i>	<i>Sodium Oxide</i>	<i>Boric Oxide</i>	<i>Equiv- alents Borax</i>	<i>Excess Sodium Oxide</i>	<i>Sodium Oxide- Boric Oxide Ratio</i>
1	0.0241	0.0161	0.0439	0.0170	1.50
2	0.0252	0.0164	0.0447	0.0180	1.53
3	0.0158	0.0100	0.0273	0.0114	1.58
4	0.0195	0.0100	0.0273	0.0151	1.95
5	0.0140	0.0099	0.0270	0.0096	1.45
6	0.0148	0.0106	0.0289	0.0101	1.40
7	0.0133	0.0078	0.0212	0.0099	1.70
8	0.0136	0.0089	0.0242	0.0097	1.53
9	0.0146	0.0089	0.0242	0.0107	1.64
10	0.0149	0.0100	0.0273	0.0105	1.49

of zinc oxide for part of the boric oxide. It was also found on substituting feldspar for quartz that an increase of alumina results in a decrease of solubility. In drying enamel No. 1, small crystals of borax and other soluble salts separated out, causing pitting of the enamel surface on firing.

In comparing plant and laboratory conditions, Danielson showed the results given in Table 38.

It is evident from these results, as would be expected, that with the longer milling time and the increased temperature of commercial milling, the solution of the enamel was much increased. It should also be noted that the amount of Na_2O dissolved almost trebled, and that of the boric oxide almost doubled, the former values. It was further shown, however, that under plant conditions pitting did not result when the soluble salts amounted to as much as twice that in this enamel.

In studying wet process cast iron enamels, Danielson found that the solubilities were greater, which he attributes to the lower silica and alumina contents and the increase in the content of lead and barium oxides.

The aging of enamels was shown to increase the amount of dissolved material, but the rate of solution of the different oxides varied

TABLE 38

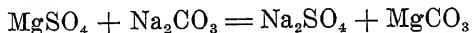
EFFECT OF MILLING CONDITIONS ON SOLUBILITY OF AN ENAMEL

Time of grinding (in hours).....	2½	8
Fineness test, grams of residue on 150-mesh screen (275 cc. enamel).....	3.50	2.75
Sodium oxide, g. per 10 cc. mill liquor.....	0.0130	0.0370
Boric oxide, g. per 10 cc. mill liquor.....	0.0078	0.0150
Borax, g. per 10 cc. mill liquor.....	0.0211	0.0409
Excess sodium oxide, g. per 10 cc. mill liquor.....	0.0096	0.0304
Sodium oxide-boric oxide ratio.....	1.67	2.47

with the time. This variation may partially explain why some enamels improve with aging, while others deteriorate. If the boric oxide increases, the enamel retains its set, but if the soda increases greatly, the enamel loses its set. An excess of boric oxide results in an enamel, which, although its set is satisfactory, tends to tear and crawl on firing. With an excess of both soda and boric oxide, there is a tendency for borax to crystallize when the enamel is drying, thus causing pitting in the fired ware. The limits for soda and for boric oxide in the mill liquor have to be determined for the particular enamel and the conditions under which it is used.

It is evident from this work, and also that of Cooke, that the soluble salts are of great importance in setting up enamels. The choice of an electrolyte depends largely on the soluble salts occurring naturally in the enamel batch. Cooke found that salts, in general, when not in the presence of other dissolved salts, do not set up enamels, the mineral acids being the only electrolytes which will function under these

conditions. He believes that there is a certain amount of chemical reaction in the slip, such as is illustrated by the equation:



This equation illustrates the effect of an addition of magnesium sulphate to an enamel which has absorbed carbon dioxide from the air and formed sodium carbonate as a soluble salt in the mill liquor.

Soluble salts have another function in enamel slips besides that of setting up the enamel; they may either promote or prevent rusting. In the granite ware industry, this is very important, as is discussed under that type of ware. In other ware, rusting is undesirable. Cooke⁸ states that sodium carbonate, sodium sulphate, sodium fluoride, sodium chloride, and sodium nitrate have little or no effect on rusting, while cobalt sulphate, sodium thiosulphate, sodium sulphite, magnesium sulphate, and acids have the effect of promoting the formation of rusting. Borax, sodium persulphate, sodium nitrite, and sodium phosphate inhibit rusting. Sodium nitrite has little effect on the set, but, in amounts as low as 0.04 per cent of the frit, it inhibits rusting.

The study of soluble salts in enamel slips will probably never be a closed chapter, because there is so much to be learned about this important subject. For the present, it is well to consider the existence of the salts and use the best methods available to control the enamel slip by testing its various properties.

Although the proper and uniform milling of an enamel is essential to good application, this is only one of the phases of the preparation of wet process enamels. The properties of enamel slips change with aging, the results depending on such factors as time, temperature, the composition and fineness of the frit, the purity of the water, and the mill additions. The aging starts with the milling and continues until the enamel is applied to the ware and dried.

Dry process enamels are ready for application when they have been satisfactorily milled and checked by firing on sample pieces.

CONTROL OF ENAMEL SLIPS

For many years the enameler had no means of accurately determining the properties of his slip. By dipping his fingers into the enamel and watching it drain and set, he was able to tell fairly well whether it could be worked or not, but he could only guess as to a remedy if the slip was not right. He was not familiar with the different properties of a slip and, as a result, was forced to judge only from general appearances. In this he did very well, but was often

⁸ R. D. Cooke, *J. Am. Ceram. Soc.*, 9, 651 (1930).

forced to use slip which was far from right, because he could not always correct it by the cut-and-try method.

The determination of the weight per unit volume soon became a common test, for it gave him some idea of the water content and how it could be corrected. He also found that, by drying a weighed sample of the enamel and reweighing it dry, he could determine the water content, but this test was slow and not commonly used.

Mobility of Enamel Slips. Many early attempts were made to determine the consistency of the enamel, but most of these were based on the assumption that an enamel slip behaved like a liquid and not like a solid. In 1917 attempts⁹ were made to study the properties of enamel slips by determining the rate of flow through two different-sized tubes. It was assumed that the ratio of the quantity which flowed through the larger tube to that which flowed through the smaller tube in a given time was proportional to the viscosity. Enamel slips, however, do not behave like ordinary liquids and these results did not help the enamer in his problem.

In 1924 Cooke¹⁰ applied the principles pointed out by Bingham¹¹ to enamel slips. Bingham showed that plastic materials under different conditions of pressure and sizes of capillaries have different rates of flow because a certain amount of force is required to start the flow of such materials. This amount of force required to start the flow was called the *yield value* and the rate of flow was called the *mobility*. Cooke, in his work, showed that enamel slips fell into this class of materials.

Consistency of Slips. The apparatus used, called a *consistometer*, consisted of a burette with a capillary tube in the bottom. The burette was water jacketed to keep it at a known temperature, the jacket being connected to a thermostatic bath. The test was made by filling the burette with the enamel slip and allowing it to run out through the capillary tube. The rate of flow was determined with a stop watch by taking the times required for the level of the slip to pass through the successive ten cubic centimeter segments along the height of the tube. The rate of flow was then calculated for the different segments. The static pressure was also calculated at these levels and the results were plotted as shown in the graph, Figure 75. The vertical axis represents the rate of flow and the horizontal axis, the pressure.

⁹ J. B. Shaw, American Clays for Floating Enamels, Trans. Am. Ceram. Soc., 19, 349 (1918).

¹⁰ R. D. Cooke, The Plastic Properties of Enamel Slips, J. Amer. Ceram. Soc., 7, 651 (1924).

¹¹ E. C. Bingham, Fluidity and Plasticity, McGraw-Hill (1922).

The points on such a graph fall in a straight line. This line, however, when extrapolated to zero rate of flow does not intersect the zero point on the pressure axis, as it would if the slip were a true liquid. The force indicated by this intersection represents the yield value for the slip under the conditions of the test. This force is the minimum pressure required to start the flow through the capillary. The slope of the line indicates the mobility or fluidity of the slip, a steep slope indicating high mobility and a gentle slope low mobility. The yield value should be such that the proper thickness of enamel will

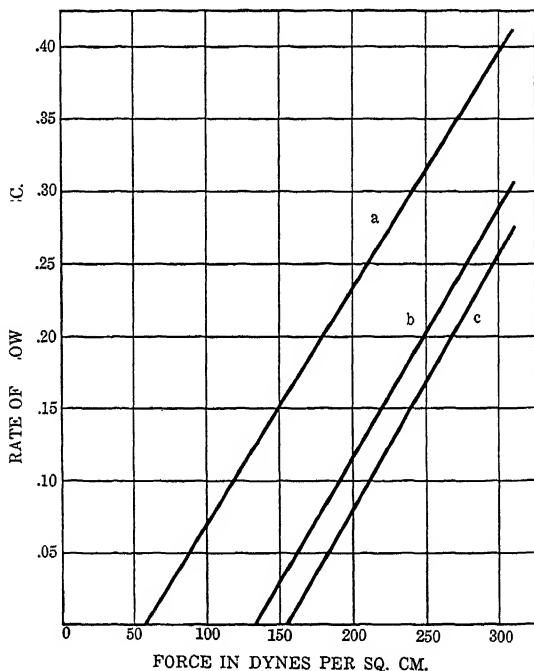


FIGURE 75. Consistometer Curves.

not flow on the ware. If too great, the enamel is commonly said to be short. A high mobility is desired, because the enamel then flows freely when above its yield value.

Cooke showed by means of these tests that: (a) an increase in temperature increased the mobility without changing the yield value, (b) an increase of the water increased the mobility and decreased the yield value somewhat, (c) an increase of the clay content increased the yield value without changing the mobility, and (d) an addition

of magnesium sulphate raised the yield value without materially changing the mobility.

This work which showed such great promise as an aid to the enameler was continued by W. N. Harrison¹² of the Bureau of Standards. Except for minor changes Harrison used the same kind of equipment as that of Cooke. The work was more refined and was very carefully controlled. The following directions for calculating the results are from Harrison:

Calculation of Results. In order to obtain the various average rates of flow for different average heights of the slip in the apparatus, it is necessary only to divide the volume of material which flows between observations by the time required. In order to obtain the corresponding shearing stresses, which are plotted against rates of flow, it is necessary to consider the average height of the slip in each particular interval, its density, and the dimensions of the capillary. The shearing stress, expressed in dynes per square centimeter and designated by the symbol F , equals

$$\frac{RhDg}{2L}$$

R = radius of capillary in cm (computed from the weight of mercury held by the tube at a known temperature)

L = length of capillary in cm (measured with a vernier caliper)

D = density of slip in grams per cubic centimeter (obtained with a pycnometer)

h = average effective height of slip in centimeters

g = gravitational const. = 981

Although greater precision can be obtained by taking into consideration internally consumed kinetic energy and surface tension, it is not probable that these values affect the accuracy of the results.

The results of a typical set of determinations are shown in Table 39.

These results show that the mobility is only slightly affected, if at all, by aging, since the lines all have about the same slope. The yield value (the distance of intersection from the zero position on the force axis) however, is decreased by aging. Thus, an enamel which has aged will require no additional water, but may need to have an electrolyte added, which will increase the yield value to that required by the work.

Plant Consistometer. To make this test applicable to plant control, it has been much simplified, as follows: Since the plant operator is interested in the properties of his slip at the temperature at which he is to use it, the tests should be made at that temperature. This condition greatly facilitates the simplification of the apparatus in that it eliminates the necessity of the water jacket and thermostatic control. The factory apparatus devised by Harrison is shown in Figure 76.

¹² W. N. Harrison, Controlling the Consistency of Enamel Slips, Bureau of Standards, Tech. Paper, No. 356, also J. Am. Ceram. Soc., 10, 970-94 (1927).

TABLE 39
CONSISTOMETER DATA

5 cubic centimeter marks	Distance in centimeters from bottom of capillary	Arithmetic average heads	Mean hydro- static heads corrected for surface tension and kinetic energy	TIME OF FLOW IN SECONDS		RATE OF FLOW IN CUBIC CENTIMETERS PER SECOND		Shearing Stress RhDg F = $\frac{2l}{2l}$
				Sample No. 1	Sample No. 2	Sample No. 1	Sample No. 2	
5	61.85	59.57	59.2	16.8	16.6	0.298	0.301	304
10	57.29	54.99	54.6	19.6	19.6	.255	.255	281
15	52.69	50.39	50.1	23.0	22.7	.217	.220	258
20	48.09	45.77	45.5	28.8	28.2	.174	.177	234
25	43.44	41.10	40.9	36.6	35.6	.137	.140	210
30	38.76	36.41	36.2	54.2	53.2	.092	.094	186
35	34.05	31.69	31.5	109.0	101.5	.046	.049	162
40	29.32	26.98	26.8	233.0	217.0	.021	.023	138
45	24.64	22.27	22.1	373.8	355.0	.013	.014	114
50	19.89							

R = 0.0812 cm. D = 1.644 L = 12.75 cm. $\frac{RDg}{L} = 5.14$

This apparatus can be constructed in any plant, inasmuch as the dimensions need not be strictly adhered to, but, once an apparatus is adopted, all comparisons should be made with the same apparatus, unless the corrective factors are considered. In normal plant tests, it is not necessary to calculate the force to dynes, but merely plot the average heights of the liquid column where the rates of flow are determined.

The calibration of the apparatus is also simple. A mark is scratched on the tube to establish the height of the upper end of the capillary tube, which should be about one inch above the rubber stopper. From this point ten cubic centimeter intervals should be determined by adding ten cubic centimeters of water at a time, until the tube is calibrated over its entire length. The distances from these points to the top of the capillary tube can then be measured with a rule and used as the values for the force axis.

Such a tube as the one described can be used for a wide variety of slips, the upper part being most suitable for thick slips and the lower part for thin slips. An average slip can be tested over the entire length. It is not usually necessary to take more than three or four points to establish the position and slope of the consistency line accurately, therefore the test is reasonably rapid.

Table 40 shows the results which were obtained by Harrison in his plant study of the ordinary tests made on enamel slips.

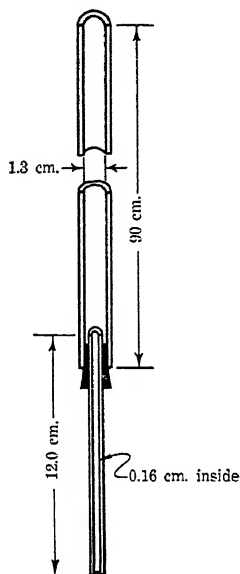


FIGURE 76.
Plant Type Consistometer.

The Gardner Mobilometer. Another instrument which has become very popular for the determination of the mobility and yield values of enamels is the Gardner mobilometer.¹³ This instrument is illustrated in Figure 77.

The principle upon which the Gardner mobilometer operates is that of forcing a disk down through the slip, which is contained in a cylinder. The force is controlled by loading the disk with known weights and the rate of movement is timed with a stop watch. Sward and Stewart's description of the test is as follows:

¹³ G. G. Sward and J. A. Stewart, Educational Bureau American Paint and Varnish Manufacturer's Association, Circular, No. 294.

The instrument consists essentially of a cylinder supported by a base plate, a plunger or piston, and a bracket to support the plunger. The plunger consists of a disk with 51 perforations $\frac{1}{16}$ of an inch (1.59 mm.) in diameter, and a weight pan attached to upper end of a brass tube. Two supplementary disks, which greatly

TABLE 40
CONSISTOMETER TESTS MADE AT PLANT PRODUCING SHAPED WARE

Kind of enamel and condition	Set, or draining period, seconds	WEIGHT PER UNIT AREA		YIELD VALUE		MOBILITY		Specific gravity	Water cent Per	Room temperature °F.
		Ounces per square foot	Grams per square meter ¹	Relative units	Standard-sized units	Relative units	Standard-sized units			
White, ready for delivery	20	6.4	1,950	21.5	130	0.133	0.113	1.918	24.0	81
White, heavy	34	7.5	2,290	30.0	181	.108	.090	1.921	23.8	83
Same, water added	20	6.4	1,950	21.6	135	.188	.164	1.892	25.2	82
Same, more water added	21	4.0	1,220	16.0	85	.253	.206	1.872	26.0	82
Same, salts added	18	6.0	1,830	22.0	133	.251	.216	1.872	26.0	82
Same, stood overnight	21	5.2	1,590	20.0	117	.211	.179	1.880	25.4	77
White, from dipping table	24	8.5	2,590	27.7	172	.107	.085	1.942	23.0	76
Same, water and salts added	20	7.2	2,200	26.0	155	.186	.158	1.892	25.2	76
Same, more water and salts added	16	7.7	2,350	27.0	165	.272	.234	1.858	26.7	76
Same, stood two hours	16	7.0	2,140	24.3	146	.247	.213	1.858	26.7	78
Limits	16-34	4.0-8.5		16.0-30.0	85-181	.107-.272	.085-.234		23.0-26.7	76-83
Ground coat, heavy	11	5.2	1,590	18.8	100	.584	.579	1.636	36.5	79
Same, water added	13	3.3	1,010	14.0	70	.708	.707	1.610	38.1	78
Same, salts added	9	4.6	1,400	17.3	93	.718	.733	1.610	38.1	78
Ground coat, heavy	12	4.2	1,280	15.5	83	.592	.594	1.643	36.1	78
Ground coat, as used	10	4.8	1,460	18.2	96	.661	.669	1.621	37.3	82
" " " "	10	4.2	1,280	17.3	93	.650	.660	1.631	36.7	82
" " " "	10	4.3	1,310	16.9	88	.775	.790	1.600	38.7	81
" " " "	10	4.2	1,280	17.7	92	.708	.722	1.621	37.3	80
" " " "	10	4.6	1,400	17.7	96	.708	.722	1.630	36.8	80
" " " "	9	4.6	1,400	18.1	97	.636	.638	1.650	35.6	80
Limits	9-12	3.3-5.2	1,010-1,590	14.0-18.8	70-100	.584-.775	.579-.790	1.600-1.650	35.6-38.7	79-82
One coat gray, as used	11	7.7	2,350	26.3	151	.438	.403	1.767	28.9	74
" " " "	11	7.7	2,350	23.3	137	.387	.366	1.773	28.6	74
" " " "	13	7.9	2,410	31.6	173	.232	.235	1.807	26.8	75
" " " "	10	8.0	2,440	27.6	163	.397	.379	1.773	28.6	76
" " " "	13	6.7	2,040	24.0	142	.273	.240	1.835	25.4	80
" " " "	10	7.7	2,350	25.2	147	.361	.341	1.775	28.4	76
" " " "	10	10.4	3,170	39.0	224	.268	.240	1.794	27.4	76
" " " "	12	7.6	2,320	27.2	157	.273	.240	1.818	26.2	77
" " " "	13	7.2	2,200	24.7	144	.332	.297	1.799	27.2	77
" " " "	12	6.6	2,010	25.6	143	.343	.303	1.796	27.3	78
Limits	10-13	6.6-10.4	2,010-3,170	23.8-39.0	137-224	.268-.438	.240-.403	1.767-1.835	25.4-28.9	74-80

¹ Figured to nearest 10 g. even.

extend its range, are supplied with the instrument. One is solid, the other has four holes 6.25 mm. diameter.

The weight of the moving system, which includes the disk, connecting tube, weight pan and lead shot in the hollow connecting tube, is 100 grams. In many cases it is desirable to use different loads on the plunger and express the results as a load-time curve.

The cylinder is filled to a depth of 20 cm. with the material to be tested. The cylinder is leveled by means of the adjusting screws. The disk end of the plunger is then introduced into the cylinder and the bracket attached. The time required for two marks 10 cm. apart on the stem of the plunger to pass through the collar is then recorded. Some operators may prefer to use a greater length of travel. This is easily done by making the required marks on the stem. The marks have previously been located, so that they pass through the collar of the bracket as the disk passes through the mid portion of the cylinder. Thus the plunger is in motion both at the beginning and end of the interval.

In performing the test, the piston is raised so that the lower mark on the rod is a few centimeters above the collar. The material adhering to the stem should be wiped off. This can be done with the thumb and forefinger of one hand, while the plunger is being withdrawn from the cylinder with the other hand.

Several loads are used and the results plotted as shown by the diagram in Figure 78.

Straight lines should be obtained when the points are plotted, otherwise the yield value and mobility would be indicated as variable quantities. If the lines are not straight, it indicates that too small loads have been employed or that the test has been inaccurately made.

As in the use of the consistometer, the slopes of the lines indicate the mobilities, and the intersections on the force axis the yield values.

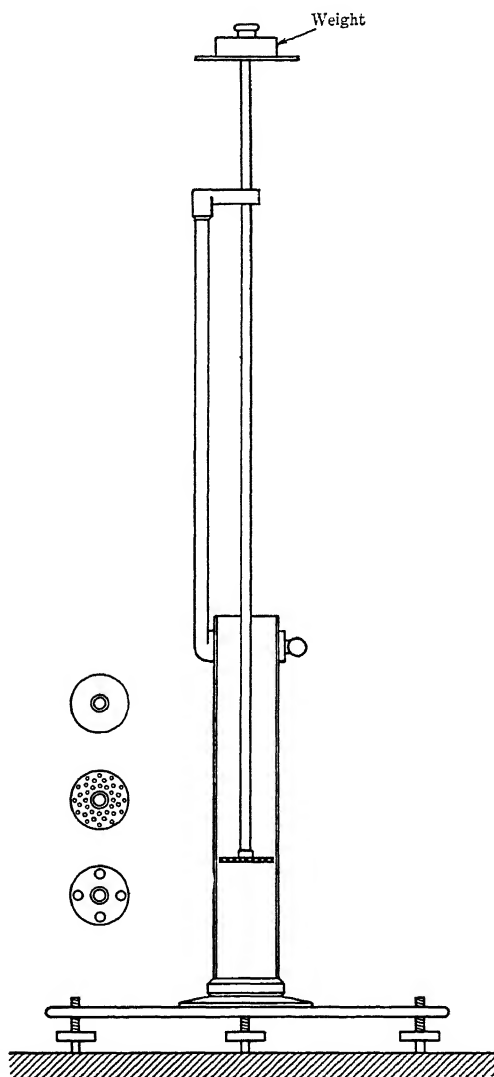


FIGURE 77. Mobilometer.

Specifications for the standard Gardner mobilometer as given in Table 41:

TABLE 41
SPECIFICATIONS FOR THE STANDARD GARDNER MOBILOMETER

Internal diameter of cylinder.....	= 3.9 cm.	} Chromium plated brass
Length of cylinder.....	= 23.0 cm.	
Thickness of cylinder wall.....	= 1.0 mm.	
External diameter of piston.....	= 6.5 mm.	} Brass tubing
Length of piston.....	= 51.0 cm.	
Internal diameter of support bearing.....	= 7.0 mm.	} Nickel plated brass
Diameter of weight pan.....	= 6.5 cm.	
Length of each side of triangular base.....	= 25.4 cm.	} Sheet brass
Thickness of triangular base.....	= 6.0 mm.	
Number of perforations in regular disk.....	= 51	} Sheet iron
Diameter of drilled perforations in disk.....	= 1.59 mm.	
	($\frac{1}{16}$ in.)	
Diameter of all disks.....	= 3.8 cm.	

In the use of either the consistometer or the Gardner mobilometer a fresh sample of the enamel is necessary for each test, because variable results will be obtained, if the same slip is used repeatedly. This effect is probably caused by thixotropy brought about by the mechanical agitation of the slip. Thixotropy is a reversible sol-gel transformation, in which the gel can be liquified and thus changed to the sol condition by mechanical agitation.¹⁴

Test for Weight Per Unit Area. A test which has proved to be very popular and useful in the industry is that of determining the weight of enamel remaining on a plate of metal dipped into it, then withdrawn, and allowed to drain. This is a simple test simulating the actual dipping of the ware and is, therefore, particularly useful in the control of ground coats. Usually a piece of sheet iron measuring 12 x 24 inches or 12 x 12 inches is used for this test. The former on the two sides exposes four square feet and the latter, two square feet of surface. By drawing such a plate through the enamel and allowing it to drain in a vertical position, the resulting weights can be duplicated quite accurately. In shop practice the 12 x 24 inch plate is considered as two square feet and is reported for example as 4½ ounces per 2 sq. ft. wet or 2½ ounces per 2 sq. ft. dry, but this really amounts to

¹⁴ E. L. McMillen, Jour. Rheol, 3, 75 (1932).

four square feet, since both sides are coated with enamel. The results of this test are in good agreement with the yield value, but are not quite as accurate a determination of this property. Since they so closely simulate actual service conditions, however, they are valuable as a control of enamel slips for slushing purposes.

Rate of Set. The rate of set is another property often measured in controlling enamel slips. Every enameler has watched the phenomenon taking place after a plate of metal has been dipped into the

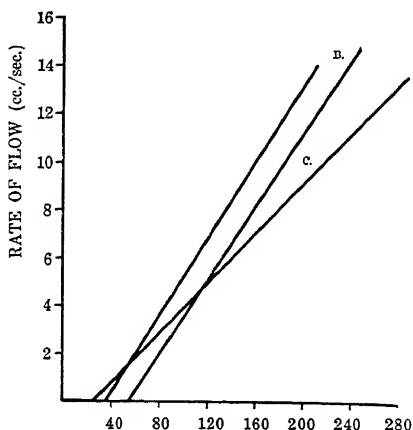


FIGURE 78. Mobilometer Curves.

slip. The enamel runs off the piece very freely until a certain thickness is reached, when it actually sets very suddenly. This set begins at the top and proceeds as a wave across the piece.

The determination of the rate of set consists of measuring, by means of a stop watch, the time required for the set to take place, after the plate is withdrawn from the slip and placed on the rack. This time of set varies over a fairly wide range and is in fair agreement with the mobility measurements. Thus, a slip of high mobility drains quickly and one of low mobility drains slowly.

Summary of the Control of Slips. The control of the consistency of enamel slips depends upon such fundamental factors as:

(a) The amount and kind of colloidal matter in the slip. This colloidal material is made up of clay particles, frit particles, opacifiers, color oxides, or other materials added to the slip. The amount of colloidal material depends upon the degree of milling and the amount of the colloidal mill additions.

(b) The degree of flocculation of the colloidal matter in the slip. This depends upon the amount and kind of salts present in the slip, including that due to solution of the frit, mill additions, or added electrolytes. Aging affects these conditions in that it allows time for solution to progress.

(c) The amount of water in the slip, which has primary influence on the mobility.

(d) The size and specific gravity of the particles, which must be suspended by the colloidal material.

These factors influence the suspension and consistency of a slip, not individually, but as a group, one depending on another. The development of a high yield value, for example, depends not only on the kind and amount of soluble salts present, but also on the colloidal content. If the colloidal content is low and sufficient electrolytes are added to flocculate it completely, a further addition of electrolytes does not bring about an increased yield value.

If the slip contains a large amount of water, the colloidal content must be increased to make possible the formation of a colloidal structure which will suspend the frit particles. In general, the larger the amount of water, the greater the content of clay needed to suspend the enamel. Likewise, if the frit is coarsely milled, it is more difficult to keep it in suspension. For this reason the colloidal content and flocculation must be greater for a coarse frit than for a finely ground enamel. An understanding of these properties of slips is necessary to an intelligent control, for the factors involved are numerous and since they change in presence of one another no set rules can be laid down for the adjustment of all slips.

It may be useful, however, to summarize briefly the more general principles of controlling the slip.

(a) The yield value is increased by an increase of clay content or the use of a more colloidal clay, by an increase of electrolytes of the proper kind (depending on the soluble salts already present in the slip) and by finer grinding.

The yield value is decreased by aging, by decrease in the clay content, and by coarser milling.

(b) The mobility can be increased by increasing the water content, or lowered by decreasing it.

(c) The set of an enamel can be controlled in the same manner as the yield value.

(d) The time of set can be controlled in the same manner as the mobility.

In general, the control of enamel slips is facilitated by uniform milling, mill additions, and aging, leaving a minimum adjustment for the slip when it is ready for use.

THE APPLICATION OF ENAMELS

The proper application of enamels is an extremely important operation for the success of the subsequent operations depends very much on it. Both the ware and the enamel have reached a stage in manufacture where they have acquired a considerable value, due not only to the material but to the work which has already been put on them. In general, an enamel should be applied as thinly as possible to obtain a complete, uniform, and good covering. Enamels of excessive thickness are usually weak mechanically and are, therefore, more likely to be damaged by bending the iron or by mechanical blows. An excess of enamel is a waste of enamel and it requires a longer or harder firing to melt it down to a good gloss.

A uniform thickness of an enamel coating is stronger and looks better than one that is irregular. Even with opaque enamels, variations of thickness affect the color and aggravate chipping or crazing. An enamel applied in a wavy condition is often wavy in the finished ware.

THE METHODS OF APPLICATION

Enamels may be applied to the metal in a number of different ways, depending on the requirements and conditions of the individual cases. Sheet iron ground coats are generally applied by dipping or slushing, since the ware is usually to be coated with the ground coat on all sides. *Dipping* is an operation in which the metal blank is immersed in the enamel slip and then withdrawn and allowed to drain. If the metal article is small and has a simple shape, this is not usually difficult, although practice is required. If, however, an article such as a refrigerator lining is to be dipped, it must be rolled through the enamel slip, so that all parts are coated, and then raised and drained in various positions to give a uniform coating. It is necessary to make a study of the dipping of such ware and by many trials arrive at the most efficient method of handling each piece.

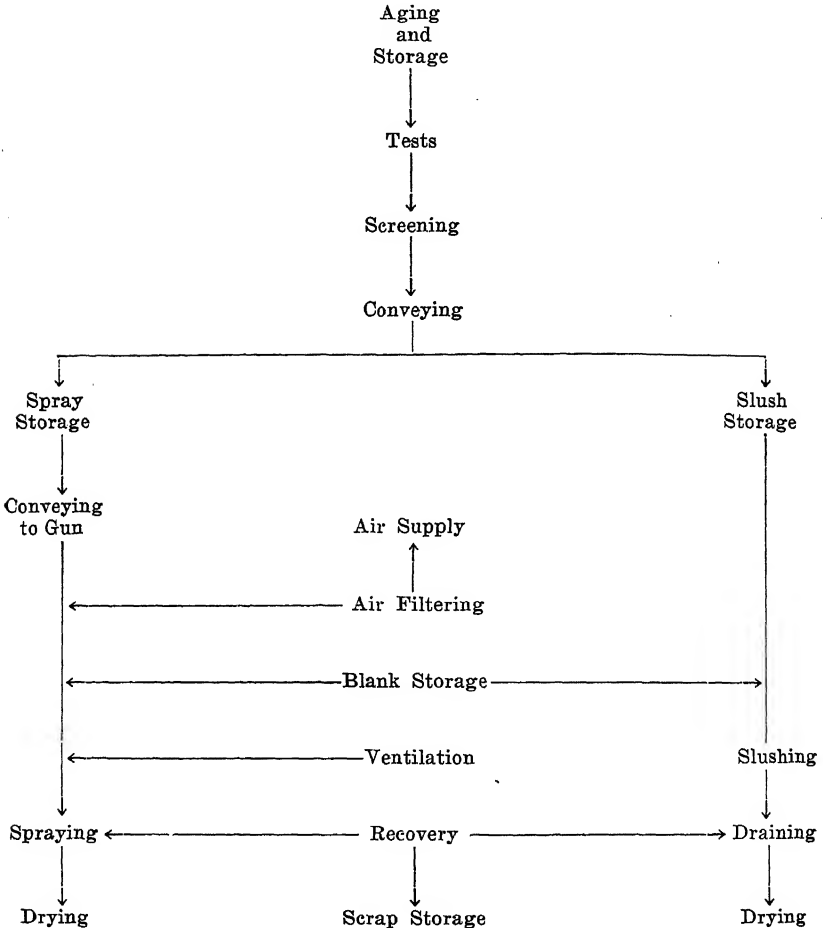
Slushing differs from draining in that the enamel slip is thicker and must be shaken from the ware. It is convenient for small odd shaped pieces, such as kitchen ware, and is used extensively for such work.

Sheet iron cover enamels are not usually dipped or slushed, but in some cases where the cover is to be applied on all sides of the shape these methods are employed.

Dry process cast iron ground coats may be either dipped, slushed, or sprayed. In this work the ground coat is very thin and watery, since it must be applied as an extremely thin coating.

FIGURE 79

FLOW SHEET FOR THE APPLICATION OF SHEET IRON AND WET PROCESS
CAST IRON ENAMELS



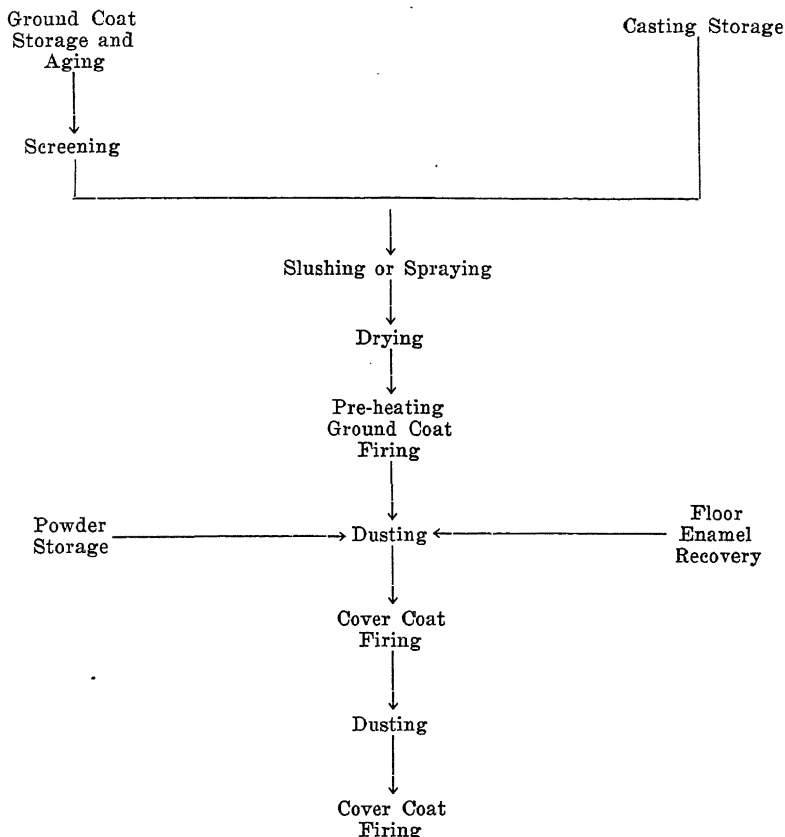
The dipping of cast iron is similar to that for sheet iron, but slushing here consists of pouring the enamel slip over the casting and allowing the excess to run off. In all these methods of application the ware must be absolutely clean, inasmuch as any grease, dirt, or

perspiration will cause the enamel slip to flow unevenly and possibly prevent good adherence in the dry condition.

Spraying is the application of enamel slip to ware by atomizing it through an air gun, whereby the fine spray impinges on the ware. It is used for most sheet iron cover enamels and wet process cast iron

FIGURE 80

FLOW SHEET FOR THE APPLICATION OF DRY PROCESS CAST IRON ENAMELS



enamels, and has the advantage of coating only the part of the ware which is exposed. When the ware is large or difficult to handle, even ground coats may be sprayed, as for example, cast iron tubs or large steel tanks.

In dry process cast iron enameling, the dusting process is used for the cover enamels. The ground coated castings are heated to the

enameling temperature and, when removed from the furnace, the dry enamel powder is dusted through sieves onto the hot ware. The enamel sinters into place and, when the ware is returned to the furnace, it melts down to a smooth surface. This process is usually repeated several times, but, in some cases where a very fusible enamel is used, one coating suffices and the heat in the casting is sufficient to melt the enamel down without a return to the furnace.

EQUIPMENT

The equipment for the application of enamels differs greatly with the method, being quite simple for dipping and slushing, but much more complicated for spraying. In any case, it should be kept in good condition and carefully handled.

Dipping. Dipping and slushing require a tank of enamel large enough to permit the immersion of the ware efficiently. It is not necessary to immerse large pieces in one operation, because they can be rotated in the enamel batch. The enamel drained from the ware or shaken off is allowed to fall into the tanks where it is re-used. To facilitate efficient operation the tank is usually made large enough so that the draining ware can be hung on racks over the tank and other pieces dipped while the draining is taking place. The tanks are generally made of galvanized iron and equipped with a drain to make possible the rapid removal of the slip, when it becomes too old for further use, and to aid in washing out the tanks.

The supports for draining are usually points mounted in such a position on a rack so that the least possible damage will be done to the coating, and that only on the back sides. The design of the tanks and racks depends upon the ware being handled; therefore, no particular type will be described. The stirring of the enamel slip is usually done by hand, although in large tanks mechanical means may be employed.

Spraying. Spraying equipment requires a spray gun, an enamel container, and a booth in which the operation is carried out. A clean source of air pressure is necessary and some means must be supplied for ventilation and enamel recovery.

Numerous types of enamel spray guns are on the market, the progress in the development of superior types having been rapid during the past few years. The primary requirements are light weight, simplicity, good atomization, a constant flow of enamel, and resistance to wear. The operation of a spray gun depends upon a flow of enamel slip through a control orifice, called the "fluid tip," and the air cap, through which the air at a pressure of 60 to 100 pounds escapes. This

air stream breaks up the slip as it leaves the fluid nozzle, atomizing it and keeping the spray within a cone-shaped area. In some cases, it is desirable to spray the ware with a flat spray, in which case air is allowed to escape through small orifices in lugs on the face of the air cap. The air from these holes impinges against the cone-shaped spray from opposite sides, flattening it out. The design of the gun, the sizes, and accuracy of the air and liquid orifices are very important, since they control the properties and shape of the spray pattern. Figure 81 shows a diagram of the essential parts of the nozzle of a spray gun for enamels. The valves for controlling the air and enamel flow are

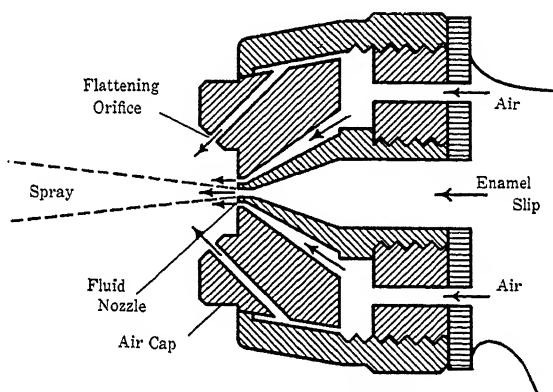


FIGURE 81. Spray Gun Head.

usually operated by a trigger which opens the air valve first and then the fluid valve.

The patterns of guns operating properly and improperly are shown in Figure 82. The pattern should be uniform in shape and the enamel should be distributed uniformly over it, with no appreciable amount of enamel being sprayed outside of the pattern. If the gun does not give a good pattern, it should be adjusted or the consistency of the enamel corrected. A tiny burr or particle of dirt in any of the orifices may cause the gun to spray a defective pattern. It may deflect the spray, causing an uneven distribution in the pattern or produce a banana-shaped, s-shaped, elliptical, club-shaped, or split-spray pattern. These conditions can be readily eliminated by careful use of a reamer or No. 00 emery cloth. Care must be taken not to deform the openings by such treatment.

An unbalanced spray may also be caused by a loose retainer ring, a poorly fitting air cap, defective packing of the plunger or air needle, or by irregular fluid or air pressure.

Some of the defects which may develop in a properly adjusted spray gun and the causes are as follows:

1. An elliptical spray is caused by the wearing away of the atomizing port and necessitates a new fluid nozzle and air cap.

2. A split spray is usually caused by burrs on the atomizing port. This is corrected by reaming this port to a perfect circle. The same condition is caused when the flattening ports become worn too large.

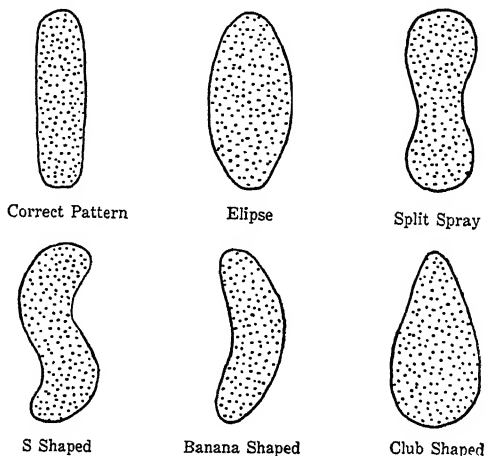


FIGURE 82. Spray Gun Patterns.*

3. An S-shaped pattern is caused by a burr on the top of one of the flattening ports and the bottom of the other. These burrs should be reamed to correct the defect.

4. A banana-shaped spray is caused by a defect in the flattening air ports and can be corrected by reaming them out. The outside of the port on the concave side of the bow should be reamed and, if necessary, also the inside of the port on the convex side of the bow.

5. When the spray is club-shaped, there is probably a burr or particle of dirt lodged in one of the sides of the central airport. If this be true, a few turns of the air cap should cause the large end of the pattern to follow around with the cap. If the large end of the pattern does not follow the turning of the air cap, the deflection is caused by a slight burr on the outside edge of the tip of the fluid nozzle. If the fluid nozzle is out of line with the gun, the defect will also appear.

6. A spray with a ragged edge indicates an insufficient atomizing or fluid pressure.

7. A spattering from the gun may be caused by (a) a loose

* W. G. Martin and A. Gruber, A. O. Smith Corp.

material nozzle, (b) a loose air cap, (c) a loose hose connection, or (d) a loose needle valve.

8. A spitting of the gun may be caused by (a) leaky air lines, (b) a loose air cap, (c) a loose piston cap, (d) a defective packing, (e) loose packing nuts, (f) dirt in the line, or (g) coarsely ground enamel.

The spray guns in an enamel shop should be given all due consideration and should be cleaned and adjusted after each day's run, and the worn parts replaced by new ones. Care in this regard will improve the efficiency of the spray department, especially if automatic or continuous spraying is used.

Enamel Supply. Three methods are used to supply the enamel slip to the spray gun: the gravity system, the pressure system, and the suction cup. The suction cup method is used chiefly for experimental spraying or when only small amounts of enamel are used. A quart cup of enamel is attached to the gun, and the suction, produced in the fluid line by the atomizing air, draws the enamel slip through the fluid tip, where it is picked up by the atomizing air and sprayed. Although convenient for a limited amount of spraying, this method is not generally used, since the cup must be frequently refilled and the weight of the cup of enamel is added to the weight of the gun.

In the gravity system a small tank of enamel is located above the spray booth, the enamel flowing by gravity through a hose to the gun. If the tank containing the enamel slip is properly constructed and kept at a constant height, the pressure is constant and the method is very satisfactory. The size of such tanks is usually limited and no provision is made for stirring. The system is, however, convenient and dependable and the cost of installation and operation is very low.

The pressure method consists of a pressure tank containing the enamel, which may be stirred by hand or by power. A pressure regulator is necessary, a gauge pressure of up to twenty pounds being used. The enamel is thereby forced from the tank through a hose to the spray gun. This method is particularly suited to large or continuous production, since it has a large enamel capacity. Many guns may be fed from the same tank, providing the line resistance does not interfere with the uniform distribution of the enamel. In such cases the enamel is usually fed to a manifold and the hoses to each gun are of equal length and tapped off the manifold.

Conditions, such as the consistency of the enamel, the type of spray gun, the atomizing pressure, the fluid pressure, and the length of hose,

all affect the spraying of enamels; therefore no definite set of conditions can be recommended.

Figure 83 shows the effect of pressure on the amount of enamel delivered for different lengths of hose, as compared with the same effect for water. Differences of length of hose become of significance when spraying at different distances from the tank.

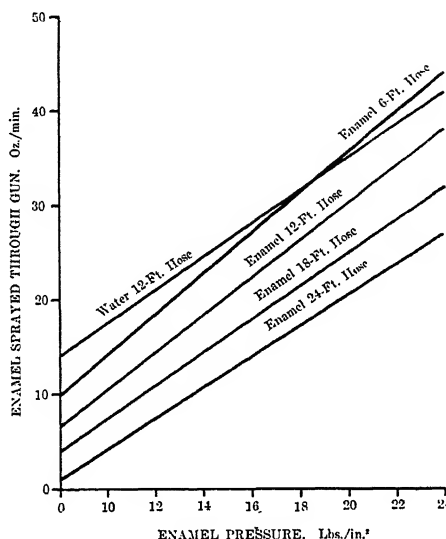


FIGURE 83. Effect of the Length of the Hose on the Pressure.*

Figure 84 shows the amount of back pressure and suction developed in the fluid line of a spray gun by various atomizing pressures. This chart shows that with the higher atomizing pressures less enamel is sprayed than with the lower pressures. A higher atomizing pressure, therefore, calls for a higher fluid pressure.

The Air Supply. The air supply for spraying must be free from oil, dirt, and water. Since the air from the compressors usually contains both oil and moisture, the air is passed through baffle tanks and air filters prior to use for spraying. Blow-off valves are used to eliminate the condensed water, much of the oil passing off with it. As the air comes from the compressor it passes into air receivers, where it cools and a large part of the oil condenses. It is desirable to keep this air cool so as to diminish its water content, but even with the best conditions filtering is necessary prior to spraying. In some cases one

* W. G. Martin and A. Gruber, A. O. Smith Corp.

large air filter serves, but current practice tends to the use of a separate filter for each air line.

The Spray Booth. The spray booth is generally a galvanized iron chamber with an exhaust system, a means for collecting the waste enamel, and the front open for spraying. It is of sufficient size to permit the convenient spraying of the ware. Some spray booths are operated continuously by having the ware carried on an automatic conveyor through the booth and from there to the dryer. In such booths two or more operators may work at the same time or in some cases, where flat surfaced ware is being sprayed, automatic spray guns may be used.

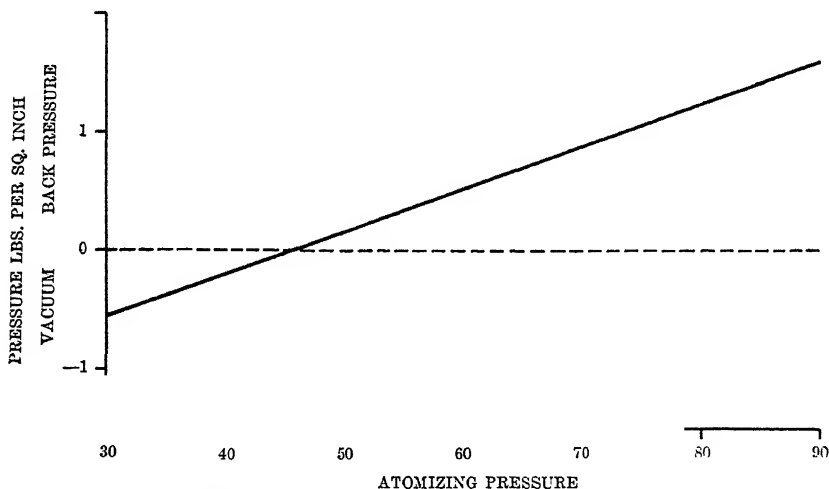


FIGURE 84. Effect of the Atomizing Pressure on the Liquid Pressure.*

The ventilator of the spray booth should be such that the air flows from the front to the back over the whole area and at as uniform a rate as possible. If the ventilating air flows through the booth unevenly, there is a tendency for the spray to be carried back to the operator. This is dangerous, particularly if the enamel is of the soluble lead-bearing type. Subjecting the operator to the spray dust should be avoided as much as possible. Another objection to an unevenly ventilated spray booth is the deflection of the spray from the spray gun when the ventilating air flows very rapidly near the object sprayed.

A properly constructed spray booth has a baffle plate between the booth proper and the ventilating duct. This plate is usually a sheet

* *Ibid.*

of galvanized iron about three inches from the exit side of the booth and extending to within a few inches of the adjacent sides. Over the surface of the baffle plate are a number of two- or three-inch holes. In many cases, two baffle plates a few inches apart are used and the holes are staggered so that there is no direct path for the air to flow through.

The design of spray booths should also permit easy cleaning and recovery of the waste enamel. The bottom of the booth is usually made so that it acts as a container for this waste, and, when the walls are brushed down, the enamel is collected therein. This enamel is recovered at the end of each day and reworked into a condition suitable for first-coat enamel. It is desirable to have a water drain in a spray booth, so that the whole booth can be washed and flushed out after recovering the enamel.

Since the recovery of enamel is important, it is necessary to have different booths for the different kinds and colors of enamels. It is possible to have these all connected to the same ventilating system but an individual fan for each booth is preferred. It is difficult to create and maintain an equal flow of air in more than a few booths by a central ventilating fan.

Dry Process Equipment. Considerable equipment is necessary for the dusting of dry process enamel because of the difficulty of handling the hot castings. The handling equipment consists of a fork for removing the ware from the furnace and a jig for holding the ware in the various positions necessary, so that the enamel can be rapidly and uniformly dusted over the surface. These jigs are often quite complicated and, since they vary with different designs of ware, they will not be described in detail here. They must, however, hold the casting securely and be able to tilt and rotate it. They may be operated either by hand or power. Two men are required, the duster and the helper, or, in the case of power-operated jigs, two dusters.

The screen-shaking machine used for dusting the enamel is called a *dredge* and consists of a round screen of 60 to 100 mesh and about ten inches in diameter, mounted at the end of a handle about five feet long. These dredges are usually vibrated mechanically by either an air or electric vibrator, which can be controlled by a button on the handle. In a few cases of small production or touching up the ware a small dredge may be used and operated by hand. In this case an egg-shaped iron ring on the end of a short handle, held in one hand, is slipped over the handle of the dredge and is vibrated up and down, striking the handle of the dredge and thereby shaking the screen.

OPERATION

The successful application of enamels by any of the various methods used requires experience and care. It is necessary to apply a uniform coating, not only over the surfaces of a single piece of ware, but from one time to another. To do this, it is necessary to have an enamel properly prepared and to conduct the operations carefully. The method of dipping and draining must be uniform from piece to piece and the spraying must be systematic. The most convenient and efficient motions must be found and then rigidly adhered to.

Sheet Iron Ground Coats. Except in rare cases sheet iron ground coats are applied by dipping and draining or slushing. To dip the metal shape it must be clean and in most cases, it is fairly fresh from the cleaning operation. It is immersed into the enamel, thoroughly wet over the entire surface, and then allowed to drain either by holding or hanging it in a convenient position. The hands should not be necessary to rub the enamel over the surface during dipping, although in some cases they are used for distributing it.

In the modern plants the ware, after dipping, is hung directly on a continuous conveyor, which takes it to the dryer. In other cases, it is drained and then placed on the dryer conveyor and, in still others, it is drained and placed on racks for drying. In the latter two cases the dipper should have a helper to handle the ware after it has drained.

Slushing enamel ware is similar to dipping, except that the operator holds the piece until he has shaken off the excess and the coating has become uniform from the motions given it in the air. It is then either set on the pins in a drying rack, on the dryer conveyor, or it is hung on the furnace conveyor. If the ware is to be mottled, it must go through carefully controlled drying conditions.

Black edging enamel is practically always sprayed on the ware. It may be applied over the dry ground coat or after the first firing of the ground coat. The former method is sometimes preferred, since the latter necessitates an extra firing for the black edging enamel.

When applied over the dried ground coat, it is sprayed very dry to avoid re-wetting the ground coat enamel. If too wet, it causes blistering. This method of applying black edging over the ground coat is satisfactory, if the ground coat is uniform and is not too thick, and if the black edging is applied dry and rather thin.

The method of applying the black edging over the fired ground coat is much easier and is used in a great many plants.

Sheet Iron Cover Enamels. Although sheet iron cover enamels are applied to kitchen ware by dipping, most of the other application is by

spraying. This is done by a systematic series of movements, spraying lightly into corners and edges. Care must be used not to double on corners by spraying around the piece. It is preferable to spray clear across the ware in a series of passes in one direction and then spray similarly at right angles to the original passes. The enamel is applied until it has a wet condition, but must not be thick enough to run.

When the cover enamel is dipped or slushed on kitchen ware, it is handled with tongs to prevent undue damage to the coating. The edge or bead is usually wiped off with a small sponge and the beading enamel is applied with the finger. This beading enamel is somewhat heavier than the regular cover enamel and is applied with the cover coat preceding the last cover coat to be applied. After applying the last cover coat the bead is wiped off, exposing the color of the beading enamel. If the outside of the ware is to have a different color from the inside, the cover enamel may be applied by spraying instead of dipping.

Wet Process Cast Iron. Wet process cast iron enamels are always sprayed and may be used with or without a ground coat. The best finish whites always have ground coats, but a great many cover enamels are applied directly on the iron.

Before applying wet process enamels to cast iron, all pits or cavities are plugged with a silicate mixture,[†] which just fuses at the enameling temperature. As with the dry process filler it must be forced into the hole to eliminate any possibility of entrapped air.

The spraying of wet process cast iron enamels is similar to the spraying of sheet iron enamels, a uniform coating being essential. Most cast iron ware is sprayed by hand.

Dry Process Cast Iron Ground Coats. The cast iron ground coats are very thin enamel slips and are applied by dipping, slushing, or spraying. The clean castings are dipped into the enamel, which is flushed over the surface to eliminate air bubbles, and then set on racks to dry. If the castings are too large to be dipped, the enamel is sometimes poured over them or, in other cases, sprayed. When spraying cast iron ground coats, several per cent of red iron oxide is often added at the mill to give the slip a red color. This aids the spraying, as it makes it easier to see where the casting has been sprayed. After the ground coat has dried, the castings are inspected and any large pits or cavities are plugged. If the cavity is large with a small opening, it is first opened with a steel punch. The plugging material is usually

[†] This silicate mixture resembles dried ground coat slip. It must have very little shrinkage and must remain porous until occluded air and moisture have a chance to escape.

ground coat, which has dried to a plastic condition. It must be forced into the holes to fill them to the bottom, since any entrapped air will expand during firing and force the material out.

Dry Process Cast Iron Covers. The dusting of dry process cast iron cover enamels requires two men, one for handling the casting and the other for handling the dredge. This operation calls for speed, as the enamel must be applied while the casting remains hot. The enamel is dusted first in the corners and then it is built up over the surfaces. As the casting cools, the enamel refuses to adhere and it must be returned to the furnace for reheating. Several coats of enamel are usually applied. Any black specks are picked out and dusted over and any beads are cut off the flanges. The dusting process requires experience, the helper being as important to good production as the duster.

DRYING AND BRUSHING

The drying, brushing, and decorating operations on vitreous enamels come between the application and firing; therefore they are grouped together. With the more recent demands for mass production and the desire for greater beauty, these operations have increased greatly in importance.

Drying. Although enamel ware can be dried in the air without artificial aid, this process is slow and, because of the variations in atmospheric conditions, the time required may vary from a half hour to many hours. In the drying of ground coats this is particularly undesirable, as the iron tends to rust with slow drying, with the resultant formation of rust spots in the enamel. In any type of ware long drying periods are objectionable because of the danger of contamination by dust floating in the air. When ware dries slowly the floor space required for the drying ware is very great and any form of continuous operation is demoralized.

It is not possible to dry the ware in the firing furnace for two reasons: In the first place enamel that is dried at too high a temperature is very likely to crack and later tear or crawl when melted down. The drying of ware in the entrance of continuous furnaces, although not in many cases too rapid, is objectionable, since the moisture collects in the furnace. If any appreciable amounts of moisture collect in the firing chamber of the furnace, it causes excessive blistering of the enamel. In some of the early installations of continuous furnaces, this difficulty was encountered and dryers were installed later.

The most desirable condition for drying enamels is the application of heat from the back of the ware so that the enamel does not have a

chance to dry on the surface first. If enamel is dried rapidly, either by the application of heat or by the circulation of air on the surface of the enamel, there is a tendency toward a surface drying while the under-enamel is quite wet. Such a condition causes a shrinkage of the different parts of the coating at different rates, and so leads to the formation of many very fine cracks that become tearing defects on firing.

It is possible to use a high clay content and a coarsely milled enamel which can be dried successfully under very severe conditions. This, however, is again objectionable since the enamel fuses to a more uniform coating, is more easily applied and has a better gloss if the milling is somewhat finer and the clay content kept at a minimum.

The drying of *granite ware* enamels requires particular care to produce the desired mottled effect. These enamels contain salts, such as cobalt and nickel sulphates, which promote rusting of the ware. To obtain a uniform mottle, it is necessary to control the drying of the ware by careful regulation of the humidity and temperature of the drying room. Thus the enamel is held in a moist condition until it has rusted sufficiently, whereupon it is dried rapidly. Many factors influence the mottling of these enamels, but the drying operation is one of primary importance.

The drying of enamels, like other materials, depends on the absorption of moisture by the air; therefore the capacity of the air for absorbing moisture is important. This property of air depends upon its temperature and its humidity, or the relative amount of moisture it contains. If the temperature of the air is increased or the moisture content decreased, its ability to absorb moisture from the enamel is increased. In humidity drying the moisture content of the air is kept high, even at the elevated temperature, resulting in very slow drying of the ware. As the moisture content then is reduced by the introduction of dryer air, the drying operation is greatly accelerated. It is thus evident that the dryer atmosphere must be continuously changed as the moisture from the ware rapidly reduces the ability of the air to absorb further moisture.

In the drying of a material, such as enamel, two phenomena are necessary to successful operation. The moisture must diffuse to the surface and it must evaporate as it reaches the surface. If the evaporation takes place faster than the diffusion of the moisture, the surface is dried first and the enamel tends to crack. This is a result of too severe drying conditions. Since the rate of diffusion increases with temperature, more rapid drying can be carried out successfully if the

temperature is increased and the humidity held at a point where the surface evaporation does not exceed the rate at which this diffusion brings the water to the surface. The method of heating the enameled ware from the back is one method of accomplishing this result and probably in most cases the most economical and satisfactory one.

Enamel Dryers. Although the use of steam pipe benches, portable blowers, and drying rooms is still common in the industry, these methods are far from efficient. The continuous type of dryer is superior, both from the standpoint of production and satisfactory drying control, because the ware can be loaded directly on the conveyor, obviating considerable handling. All the ware is subjected to the same drying conditions and the hardness of the coating is more uniform, which is important when brushing is necessary.

There are numerous designs for continuous dryers, but all are essentially long chambers with a continuous conveyor traveling through them and with the radiated heat or hot air introduced from the floor. It is common practice to use the waste heat from the furnaces and, by means of an interchanger heat the air which is circulated by a fan through openings in the floor of the dryer.

A longitudinal combustion chamber under a muffle floor is sometimes used and, in other cases, gas or electricity is used as direct heat at the floor of the dryer. The necessary change of air may be accomplished by natural draft, by a circulating fan, or, as is common, by the circulation of air through the ends of the dryer.

Dryers need not be of heavy construction, but should be well insulated to conserve heat. The waste-heat dryers usually operate at temperatures of about 200-300° F while the direct-heat or muffle dryers generally operate at from 300-400° F. With these temperatures prevailing in a properly constructed and ventilated dryer, it is possible to dry ware successfully in from three to five minutes.

Increased attention to drying has greatly improved enameled ware, and is one of the necessary steps in continuous operation.

Brushing. The most satisfactory and generally used method of producing more than one color on a single enameled piece is that of brushing. The dried enamel, applied over the previously fired coat of another color, is brushed off from areas where it is desired to show the color of the previous coat. Thus, for example, in the production of black edging on a white panel the white cover coat is sprayed and dried, after which it is brushed off along the edges of the panel, where it is desired to show the previously fired black edging enamel. This

brushing operation may be extended to many different colors, such as are used in commercial signs.

For successful brushing the enamel must not be applied too thickly; it must be uniform and it must be dried without the development of a brittle structure. The adherence to the previous coating must be good, the enamel must be sufficiently hard to withstand handling and yet soft enough to permit easy brushing. The clay content in the enamel usually produces the proper hardness, although in some cases other agents, such as gum arabic, are added.

Gum arabic is usually prepared by soaking the dry gum for about ten hours with twice its weight of water, boiling, and then sieving to remove any lumps that may not have dissolved. A few cubic centimeters (not over five) are then added per gallon of slip and thoroughly stirred in. An excess of gum not only makes the enamel dry too hard, but it may cause blistering and discoloration of the enamel. Enamel treated with gum must not be left from day to day, as it has a tendency to lose its set. This is due to the protective colloid action of the gum. On long standing the enamel becomes lumpy and useless. Because of these characteristics the use of gums is limited to cases where they are necessary to obtain sufficient hardness. Ammonium alginate, gum tragacanth, and dextrin have also been used for this purpose.

The brushing of enamels is a hand operation, although many attempts have been made to use machines. For black edging, hand brushes are quite commonly used with guides, so that one or two sweeps of the brush give a clean border and straight edge. In other cases rotating brushes are used, but even by this method the ware must be manipulated by hand.

For the making of signs, it is a very common practice to use stencils and to brush off the dried enamel exposed through them. Many attempts have been made to spray through stencils, but in most cases they have been unsatisfactory, as the enamel tends to creep under or build up along the edges of the stencil.

The making of stencils for brushing vitreous enamels requires practice and careful planning. Twenty-five to thirty gauge sheet zinc is generally used, although brass is satisfactory and, if the stencil is to be used only a few times, a heavy paper can be used. The stencils may be made by either cutting with a sharp chisel or etching.

To cut a stencil, the sheet of zinc is first sheared to the proper size with a sufficient margin for holding it in place during the brushing. The design is then laid out with a sharp pointed steel pencil. Ties must be left for holding the centers of such letters as O, D, P, R, etc. in place.

The sheet of zinc is then placed on a flat metal surface and cut with sharp chisels. The edges are smoothed off with fine files. A second stencil is necessary to brush the spaces left in the ties of the original. This is made in a similar manner to the first. In simple two-color signs two stencils are all that are necessary, but for more complicated signs a considerable number must be used.

The etching process of making stencils consists of coating the zinc on both sides with an asphaltum paint and laying a sheet of lead foil over one side. This is rolled down smooth and the stencil laid thereon. The stencil is then traced in the lead foil with a sharp knife. The asphaltum is washed out of the open spaces with a solvent, such as turpentine. The stencil is then placed in a bath of dilute hydrochloric acid (muriatic acid) until the exposed zinc is dissolved away. It is then removed and washed in a solvent to remove the remaining asphalt paint and the edges are smoothed with files. Two or more stencils are necessary to take care of the ties which must be left to hold the stencil together.

In the brushing of stencils considerable dust is evolved, so that the workmen must be protected by adequate ventilation. Attempts have been made to equip the brushes with a suction similar to that used on vacuum cleaners, and in some plants this has been entirely satisfactory. Booths are not satisfactory; they are in the way and do not draw off the dust as rapidly as is necessary. One very successful method of removing the dust is that process using both gravity and suction, known as the "brushing table." The brushing table has a smooth screen top, through which the dust falls with a suction drawing the air down into the table. The more modern tables have slots or pockets along the outside edges, which catch the dust falling from the table. With good air flow these brushing tables are very satisfactory; they prevent the dust rising to the level of the workers' faces and carry it away as fast as it is formed.

DECORATION

The methods used for the decoration of enamels include screening, decalcomania, printing, graining and marblizing, stippling, polytone, and miscellaneous methods, such as photography and hand decoration. Such decoration may be for the purpose of increasing the beauty, utility, or merely for placing the trade mark or name on the ware.

Screen Process. The brushing process is costly from the standpoint of labor, the amount of enamel wasted, and the numbers of firings necessary to produce complicated designs. It is, therefore, not surpris-

ing that many attempts have been made to substitute other methods for obtaining the same results. The most promising and successful of these, which at the present time is used in only a few plants, is that of forcing an enamel paste through a silk or metal lawn onto the ware. Two processes are used in making the stencil. The older method consists of gluing an oiled paper stencil onto the 80 to 100 mesh silk lawn. The newer method consists of impregnating the lawn with a light-sensitive gelatin, and exposing to a bright light through an opaque stencil. The part of the gelatin exposed to the light is insoluble, while that not exposed is soluble. The development of the lawn by washing thus gives a stencil impregnated in the silk lawn.

The enamel must first be made into a thick slip with an oily material such as butyl acetate, by milling to extreme fineness between 200 and 300 mesh. To apply the enamel, the lawn is laid over the piece to be enameled, the slip is placed on the lawn, and, by means of a rubber squeegee, it is forced through the part of the lawn not covered by the paper or gelatin. If a fine lawn is used and the enamel is properly prepared, the design does not show the weave of the lawn. The advantage of this method is that many different colors can be applied and fired at one time, which results in a considerable saving. The amount of enamel used is small compared to the brushing process and the labor required is not great. The enamel by this process is applied very thin and must, therefore, be strong in color and opacity, which is difficult to attain with good gloss. It is more costly to mill the enamel to sufficient fineness for the silk screen process, but the waste dust of the brushing process is eliminated. It is quite probable that the process will become more popular as its development becomes more complete. Using the gelatin stencil it is possible to reproduce almost anything which can be photographed, the half-tone being readily obtained.

Decalcomania. Decalcomania, commonly called "decal", was first introduced in the United States from Germany in 1880, when it took the form of transfer papers used by children to decorate their books and toys with pictures. The industry, however, was not slow in adapting these colored decals to many articles on the market.

At the present time there are two kinds of decalcomania, the oil color decals used on painted and varnished surfaces and the ceramic decals fired on ceramic ware. These ceramic decals were first introduced by the Germans, but later were improved by the French. They have been in use on vitreous enamels in the United States for only

twenty years, although previously introduced to the glass and white ware industry.

The ceramic decal is made up of oxide colors and a flux and is actually fused into the surface of the enamel and made permanent. This is the common type used for vitreous enamels, although where permanence is not required the oil decals are sometimes used.

The making of ceramic decals is quite different from the making of oil-color decals although both use the lithographic stone. This stone, which is imported from Bavaria, is a particularly fine grain limestone especially suitable for the purpose.

The oil decal is made by grinding the pigment in an oily varnish and then printing it on the paper by the lithographic process. The color oxides of the ceramic decals are not ground with the varnish, but are dusted onto the varnish, which is first printed on the paper. This varnish covers only the surface to be colored with that particular oxide. As the varnish dries, a part of the color oxide becomes fixed, whereupon the excess can be dusted off and the design obtained.

In the making of the ceramic decals it is necessary to use a separate lithographic stone for each color, as the ceramic oxides do not blend to give an intermediate, as paint colors do.

The enameler obtains his decals from the manufacturer and is only concerned with the successful application, for which purpose several methods are employed. In the most common method, a sizing or varnish is first applied to the enameled surface with a camel's hair brush and allowed to dry to a tacky or sticky condition. The decal is then applied and rolled down and smoothed with a damp sponge. The ware is next immersed in water until the paper works loose, when it is rinsed off under a stream of water. It is necessary that sufficient time be given to soak off all of the excess varnish, after which the ware is allowed to drain and dry. In some cases, where the water has considerable mineral content, it is necessary to wipe the surface dry with a piece of cheese cloth. The ware will become stained in the firing process if varnish or dirty water is left on it.

After drying the decal two different procedures may be followed: the ware may be either baked at 400 to 450° F and then fired or it may be fired direct. The former process is preferred, because there is less danger of defects developing. In the baking operation the varnish is evaporated to a brown powder, which is burned out in the firing operation.

In some cases the decal is applied without sizing, in which case it is pressed down on the enamel surface and soaked with a damp sponge

and roller. The paper is then lifted off and the design again pressed down with the damp roller. This method requires more careful technique in application, but it eliminates the sizing and baking operation.

The application of decals to wet process cast iron is more difficult than to sheet iron because of the tendency of the former to blister. The use of a ground coat enamel, however, greatly reduces this hazard. In some cases the decals are applied directly to the warm castings without any sizing, but in other cases the sizing is used.

The use of decals on enameled ware has become very common and for very intricate work, they are used on signs. The preparation of the lithographic stones is costly, therefore the use of decals in small quantities is practically nil, but, where large quantities of a particular design are used, the unit cost is low.

Printing. The printing process is used extensively throughout the enameling industry because it is particularly well suited to small lettering and designs, such as trade marks, control dials, and tables, and it has largely replaced the old method of hand lettering and decoration. Printing is nearly always used after the last finish coat has been fired, although in some cases it is applied over the dried finish coat. In the former case, an extra firing operation is required, while in the latter it is fired with the finish coat.

In the semi-hand method of printing, a rubber stamp picks up the color oxide or ink from a glass plate and transfers it to the ware. This method is suitable for small production and simple printing.

In another simple method an adhesive varnish or sizing is transferred to the ware in a similar manner and the color oxide is dusted over the sticky surface. Since this color oxide only adheres to the surface coated with adhesive, the design is distinctly brought out. The varnish burns out of the coating when it is heated in the final firing.

If production warrants the initial investment, more complicated processes are used. In one process the design is engraved on a steel die, the letters being depressed, forming an intaglio plate. The ink is then spread over the plate and slicked off with a squeegee. This leaves ink only in the depressions from which it is taken up by a rubber pad or roller. The pad or roller then transfers the ink to the surface of the ware. In some cases regular printing presses especially adapted to the work are used.

The ink after printing must be dried and then fired into the enamel surface. If several colors are used, it may be necessary to make a separate firing for each, especially if they do not fuse in at the same

temperature. In such cases those fired at the higher temperatures are applied first.

Graining and Marblizing. Graining and marblizing are decorative finishes applied over the last cover enamel to give the ware the appearance of wood or marble. The processes have been extensively used and for certain types of ware, very attractive effects result. Wood graining preceded marblizing and is more extensively used. Two different methods are employed, the direct method and the indirect method. The direct method is similar to printing in that the grain is applied by inking a roller bearing the design of the grain. The necessary equipment includes the roller bearing the grain design, a flat glass plate for inking, and a smooth roller for applying the ink, or "graining paste" as it is called, uniformly to the glass plate. The operations consist of inking the glass plate and rolling the paste to a uniformly thin layer. The graining roll is then run over the surface of the plate, picking up the ink. This is then transferred to the ware by passing the graining roll over the ware.

The condition of the graining roll and the graining paste are very important. The paste is usually prepared with an oil, such as clove oil, and consists of color oxides and fluxes to give the proper color and gloss. The graining roll which is coated with a rubber-like material, consisting of gelatin, glue and zinc oxide, is prepared by casting this material on a previously prepared wood surface. To bring out the grain of the wood, it is treated with either caustic soda solution, oxalic acid, or glacial acetic acid. These materials dissolve the gums out of the wood and produce a surface greatly exaggerating the grain lines. Sometimes a wire brush is also used. After the coating is melted and cast on the wood grain surface it is removed and glued on the graining roller. The graining roller should be kept clean and should not be subjected to either a high or low temperature. When not in use, it should be oiled and supported, so that it does not rest on the graining surface. The graining roller may be of any convenient size, being operated by hand, where production is small, or by machine, when production is great.

The indirect, or offset, method of graining differs from the direct method in that the graining roll has a smooth coating and the grain is taken from an engraved plate or directly from the wood surface. An engraved copper plate is most commonly used, although a steel plate is more permanent.

The equipment necessary is the smooth composition roller, the plate with the desired grain, and a scraper or spreader. The operation

consists of inking the engraved plate with a brush and removing the excess with the scraper. The smooth roll is run over the inked plate and then rolled over the ware to be grained, thus transferring the design.

Many methods are used for the graining operation, including the hand process and that in which an automatic press is used.

After the grain is applied it is dried and fired in the regular enameling furnace. It is, thereby, fused into the enamel surface and is as permanent as the enamel itself.

Marblizing. Marblizing is similar to the wood graining processes, inasmuch as both the direct and the indirect methods are used. The latter method, however, is much more common at the present time.

The making of the marble design has required a great amount of development and much of the early work lacks quality and warmth. The more modern method, however, where the design is taken from the natural marble, gives a very beautiful finish. The marble used for graining must be selected so that it can be either etched, or sand blasted with a very fine sand to reproduce the natural design.

The graining and marblizing processes have greatly increased the field of enameled products, for they give a durable finish, which can be used for building fixtures and panels, where a plain color or mottle is not suitable.

Stippling. A stippled finish is one in which enamel of different colors is spattered on the surface of the ground coat to give a mottled finish. This effect is produced in a number of different ways. The oldest method of producing this effect is that of dipping a brush, similar to a floor scrubbing brush, into enamel and then drawing a scraper over the bristles, thus spattering the enamel on the ware. A modification is the use of a cylindrical brush which dips into the enamel and rotates past a scraper.

A third method, used extensively abroad, is that of dipping a sponge into the enamel, squeezing out the excess and then lightly touching the surface to be decorated. By careful selection of the sponges used, and practice, a uniform finish can be produced.

The more modern method uses a modification of the spray gun, in which the enamel is spattered, rather than sprayed, on the ware. By this means several colors can be applied at one time and the uniformity of the coating can be nicely controlled.

Polytone. The polytone finish is one of the most recent methods of decoration and is particularly suited to flat ware. The finish coat enamel surface is roughened up, either by spraying it very dry or by

spraying a coarsely milled enamel. While in the dry condition another colored enamel, milled very fine, is sprayed onto this dry coat from the end of the ware. This latter enamel coats only one side of the projecting particles of the rough coat. The finish is then fired to a smooth surface. This gives the enamel an appearance of having a slightly roughened surface although it is in reality smooth.

Miscellaneous Finishes. Other decorative finishes are used, but are not of sufficient importance for description here. The ceramic photograph is one of the more important as it has a very useful field in art work. X-rays affect the color of enamels and could be used for design; hand painting and decorating are used and other finishes will probably be developed.

CHAPTER 11

Firing (Burning) and Furnaces

The word firing¹ has been adopted by the American Ceramic Society as the proper term to use for what is commonly called burning in the enameling industry. Therefore, the term firing has been used in this book, except where the meaning might not be clear.

All enamels must be fired on the ware to melt them down to a smooth continuous glassy layer. The temperatures and times required vary with the different compositions and types of enamels, but it is safe to state that they are all fired at temperatures above a red heat. Since firing is the last operation in enameling, successful firing is of primary importance, for ware lost in the firing represents a loss of both the materials involved and also the labor expended on all of the enameling operations.

The requirements for the successful firing of enamels are comparatively simple. Given a good enamel, properly applied to good base metal which has been properly prepared, the following are the main firing requirements:

- (a) proper firing temperature and time
- (b) proper support of the ware
- (c) uniform heating and cooling of the ware
- (d) an atmosphere free from dust and very low in sulphur and water vapors.

Some enamels require an atmosphere containing free oxygen, but, since air consists of about one-fifth oxygen, this requirement is usually met.

Table 42 shows the common ranges of the fusion temperatures and times for the various types of enamels. These ranges hold true only for typical compositions and ordinary conditions.

The firing times and temperatures for an enamel depend upon many factors, such as: the thickness and uniformity of the metal stock, the thickness of the enamel coating, the fineness of the enamel, the resulting product desired, the ratio of the amount of ware to the reserve heat in the furnace, the weight and construction of the burning (firing) tools, the position and shape of the ware, the amount of preheating, and the radiating properties of the furnace.

The support of the ware in the furnace must be such that the ware does not become distorted in shape. The supports must not greatly influence the heating of the ware and should absorb a minimum of heat from the furnace.

¹ Bul. Am. Ceram. Soc., 12, 30 (1933).

Uniformity in the heating and cooling of the ware is of great importance for the prevention of chipping, warping, and cracking. The rate of heating or cooling is not very important, but a rapid rate usually brings about uneven heat distribution. Some enamels can be actually quenched from furnace temperature, if the uniformity of cooling can be controlled. Large enameled pipes forty feet long by thirty inches in diameter are quenched commercially from the furnace temperature to 800° F in order to raise the strength of the steel and to inhibit the tendency to fishscale.

On one occasion ² sheet iron enamel ground coats were fused by passing an electric current through the iron and thereby heating it almost instantaneously. This gave the enamel a nice coating, but the temperature had to be held for about a minute to enable the heat from the iron to penetrate the enamel, which has a relatively low thermal

TABLE 42
FIRING TEMPERATURES AND TIMES

	<i>Temperature</i>	<i>Time</i>
Sheet iron ground.....	1500-1600° F	1-4 minutes
Sheet iron cover.....	1450-1550° F	1-3 minutes
Wet process cast iron.....	1150-1400° F	10-15 minutes
Dry process cast iron.....	1550-1700° F	1-5 minutes

conductivity. Although the enameling was done in this case as rapidly as the heat could be absorbed by it, the enamel coating was of good quality. This shows that enamel ware can be fired very rapidly, if it is heated uniformly. The time required to melt the enamel down and give adherence makes the use of the electrical resistance method of heating uneconomical, even for ware of uniform design.

The atmosphere of enameling furnaces must be free from dust and dirt particles, which are likely to fly about and spot the ware. Sulphur gases in amounts as low as twenty parts per million, or .002 per cent, will cause a pronounced scum on some enamels. Water vapor in an enameling furnace causes severe blistering of most sheet iron enamels.

PHYSICAL AND CHEMICAL CONSIDERATIONS

The firing of vitreous enamels involves not only the fusing of the enamel but many accompanying chemical and physical changes. Take for example, the sheet iron cobalt ground coat, which is applied by the wet process. If the iron does not already have a thin coating of rust, such a coating develops before the enamel is dry. This rust is brownish

² W. G. Martin, A. O. Smith, Corp.

red in color and is probably red oxide or hydroxide of iron. In the early stages of firing the hydroxide decomposes and the ferric oxide produced is reduced to the black oxide of iron. As the fusion of the enamel progresses, this black oxide layer, which resembles iron scale, gradually disappears and the blue color of the cobalt glass changes to the characteristic green of an iron containing glass.

Gas Evolution. Gases are evolved through the surface of the enamel, after which the glass melts down to a smooth layer containing many small gas bubbles. These gases probably originate from the iron, the enamel, and any reactions taking place at the inter-face of the enamel and the iron. Lucian and Kautz³ found by a spectrographic analysis that the gases evolved from enameling iron below 1200° F were hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen. Between 1200° F and 1600° F they were carbon monoxide, carbon dioxide, and nitrogen. The gas evolved from a ground coat at 1500° F is principally water vapor.

Adherence. To develop adherence in sheet iron ground coats, available oxygen is necessary.⁴ This must come from either the atmosphere or some oxide at the surface of the metal. A thin layer of rust seems to aid the adherence when other oxygen is not available. It is interesting also to note that this rust layer disappears, if it is in contact with the iron, but, if suspended in the enamel glass, it remains without visible change after firing.

A microscopic examination of a ground coat enamel shows the presence of many bubbles and, if properly fired, these bubbles are small and uniformly distributed. If the enamel contains other color oxides than cobalt and manganese, it is often opaque, which obscures the bubbles, or it may show a clouded area at a depth approximating the inter-face between the enamel and the iron.

On observing the firing operation through a microscope the phenomena become quite interesting. The first visible effect is a microscopic tearing or cracking of the surface of the unmelted enamel. As the temperature increases it begins to ruffle up and melt with a wavy appearance. The surface smooths off and appears to be a clear glass. Soon, however, bubbling starts and becomes violent, the bubbles rising to the surface and bursting. Many sizes of bubbles are in evidence, but the large ones are soon eliminated and a great many bubbles of nearly uniform size remain. The enamel is properly fired at this stage. With continued firing, these smaller bubbles gradually rise to the surface

³ A. N. Lucian and Karl Kautz, *J. Am. Ceram. Soc.*, 17, 167 (1934).

⁴ R. D. Cooke, *J. Am. Ceram. Soc.*, 7, 227 (1924).

and burst, until the glass becomes clear and free from bubbles. The enamel at this stage is over-fired and will tend to fishscale. With still further firing, the enamel seems to flux with the iron and form a slag.

Observations of cross sections of the iron and enamel have contributed much to our yet incomplete knowledge of the mechanism of sheet iron ground coat firing and adherence. R. M. King⁵ describes dendrites, which he believes to be alpha iron, projecting from the iron surface into the enamel layer. These are formed by long firing periods and may be of sub-microscopic size in ordinary commercial ware. Cross sections also show crystals of iron oxide in the enamel and frequently cracks, which run parallel with the surface.⁶ The bubble structure shown by the cross section of properly fired enamels consists of small bubbles uniformly distributed.

Reboiling. On reheating the sheet iron ground coat there is often another boiling, as the ware reaches a temperature of 1100° F. which is called reboiling. The exact cause of this is not yet known, but it certainly involves physical or chemical changes in the enamel.

The following is a summary of the observations of many investigations compiled by J. O. Lord.⁷

(1) Reboiling takes place only on cobalt (and possibly nickel) ground coats and only on sheet steel (or sheet iron).⁵

(2) Reboiling commences suddenly, as the piece reaches a dull red heat, lasts for a few seconds, and then subsides and will not occur again until the piece has been first cooled nearly to room temperature.⁵

Note: Hayes, Canfield and McGohan note that "metal which reboils when enameled in the usual manner does not reboil if not allowed to cool below 500° F."

(3) Electrolytic, vacuum-distilled iron reboils very slightly for one or two heatings only.⁹

(4) Enamel may possibly reboil on copper, but only very slightly.⁵

(5) Experiments recently conducted in the laboratories at Ohio State University fail to show any reboiling in enamels applied to platinum and gold.

(6) If the piece be (a) dipped, and one side brushed off, reboiling will not occur; (b) sprayed on one side only, reboiling will occur; (c) sprayed on both sides and one side brushed, reboiling will occur; (d) sprayed on both sides and

⁵ Papers on Mechanics of Enamel Adherence: (a) J. O. Lord and W. C. Rueckel, I, J. Am. Ceram. Soc., 14, 777-81 (1931); W. C. Rueckel and R. M. King, II, *ibid.*, 782-88; W. K. Carter and R. M. King, III, *ibid.*, 788-94. (b) A. McGreaves-Walker and R. M. King, IV, *ibid.*, 15, 476-80 (1932); G. H. Spencer-Strong and R. M. King, V, *ibid.*, 480-83; K. Schwartzwalder and R. M. King, VI, *ibid.*, 483-86; G. H. Spencer-Strong, J. O. Lord, and R. M. King, VII, *ibid.*, 487-90. (c) R. M. King, VIII, *ibid.*, 16, 232-38 (1933). J. Am. Ceram. Soc., 15, 488 (1932)

⁷ A. Hayes, J. J. Canfield and G. W. McGohan, J. Am. Ceram. Soc., 15, 338 (1932).

⁸ J. Am. Ceram. Soc., 16, 442 (1933).

⁹ Anson Hayes, J. J. Canfield, and G. W. McGohan, Reply to Schaal and Fuller, J. Am. Ceram. Soc., 15, 351-53 (1932).

⁶ R. M. King, Mechanics of Enamel Adherence, VIII, *ibid.*, 16, 232-38 (1933).

one side brushed and then sponged clean, reboiling will not occur.¹⁰ In general, pieces enameled or coated in any manner on both sides show greater tendency to reboil than when enameled on one side only. A complete description of this behavior is, however, very involved^{9,8}

(7) Sandblasting the surface of the sheet seems to increase the reboiling tendency, particularly if only one side is sandblasted, whereupon that side will reboil.¹⁰

(8) If the piece is fired in vacuo, it will not reboil in any subsequent firing.⁹

(9) As much as 10% carbon dioxide has been found in the gases produced when reboiling takes place.¹¹

(10) After twenty-three to twenty-five heatings, no further reboiling takes place.⁹

(11) When, after initial firing, the piece is cooled in the furnace, reboiling will not occur on the next heating. Furthermore, slow heating reduces or eliminates the reboiling tendency.⁶

(12) Pieces reboil more, if allowed to rest for several days or longer after the original heating.¹⁰

(13) Simple glass enamels, without cobalt or nickel, do not reboil.⁵

(14) Some steels reboil more than others.¹²

(15) So far no serious reboiling tendency has been found where there is no evidence of the metal dendrites observed by Schwartzwalder and others.

The matter of reboiling is receiving considerable attention and new facts are constantly being accumulated. Some of the data point to a mechanical, and some to a chemical explanation for reboiling. Microscopic observations by both J. O. Lord and the author during the actual reboiling of the enamel have shown exactly how the bubbles appear. On heating a sample from room temperature, the specimen first appears as a glass containing many small bubbles uniformly distributed and of fairly uniform size. As the temperature increases, highlights appear, caused by a bulging of the surface of the enamel. As heating is continued, these bulges or large blisters become very distinct, the whole thickness of the enamel layer being raised from the iron. As they become larger they round themselves and then a bubble is seen to penetrate the lower surface of the enamel and slowly rise to the upper surface, where it finally bursts. The enamel is then drawn into this cavity and smooths over. This small area is free from the ordinary enamel bubbles, probably being fined by the flowing action. These reboiling bubbles are much larger than any of the bubbles formed during the original firing. The whole layer of enamel rises as though the gas collected first between the enamel and the iron.

¹⁰ Personal communication by W. H. Pfeiffer and H. W. Alexander, February 6, 1933.

¹¹ A. I. Andrews, An Oral Discussion of Papers on Reboiling at the Annual Meeting, American Ceramic Society, Pittsburgh, Pennsylvania, February, 1933. A. I. Andrews and R. E. Mullady, Further Data on Reboiling, *J. Am. Ceram. Soc.* 17, 346 (1934).

¹² R. B. Schaal and D. H. Fuller, Modern Enameling Troubles, *Ceram. Ind.*, 15, 605-14 (1930).

Evidence of this is indicated by the irregularity of the original shapes of the large blisters which later become round.

These results indicate that the reboiling blisters are not formed from the many bubbles already present in the enamel, but between the enamel and the iron. The whole thickness of the enamel is lifted up where a reboiling blister forms and the small bubbles can be seen long after the reboiling blister has started to take form.

The mill additions to enamels contain clay, which is decomposed, and water, which is vaporized. The non-volatile constituents are dissolved in the glass and the electrolytes are decomposed or dissolved in the enamel. If sulphates are present, they form immiscible liquids, which come to the surface of the enamel and, when cool, absorb water and form a scum.

Sheet Iron Cover Enamels. The firing of sheet iron cover enamels does not involve as many changes as the ground coat, since there is no interaction with the steel. The cover enamel, however, contains a greater percentage of mill additions and it must fuse into the previously fired ground coat. The contact surface between the cover coat and the ground coat must be an interfusion of the two enamels, which requires that they (wet each other) have an inter-facial tension for each other. The ground coat preferably has a slightly higher firing temperature than the cover enamel. The ground and cover enamels must have similar physical properties, such as expansion coefficients and strength, so that they will retain their intimate contact on cooling. If the cover enamel glass does not wet the ground coat glass readily, crawling and beading will result.

The mill additions of the cover enamel include an opacifier such as tin oxide or zirconium oxide, which must disperse in the glass to give good opacity. The nature of the grains of opacifiers and the composition of the glass influence this dispersion. The cover enamel does not boil violently, as the ground coat does, although there may be evidence of reboiling of the ground coat. If the reboiling bubbles are large, the blue ground coat may push through the cover enamel, producing a defect which appears as black specks.

The cover enamels are melted down to a smooth coating and when properly fired produce a high gloss and pleasing color or opacity. Colored cover enamels are often sensitive to reducing gases because of the reducible color oxides. Temperature also affects color, therefore, the firing of colored cover enamels must be under careful control.

Wet Process Cast Iron Enamels. Wet process cast iron enamels may be applied with or without a special ground coat. If a ground

coat is used, it does not contain easily reducible oxides; therefore the blistering during the firing operation is kept at a minimum. Cobalt is not necessary for good adherence, but it is sometimes used. Since wet process cast iron enamels are applied to castings, the mass of the iron to be heated is much greater than when firing sheet iron enamels. This necessitates a longer firing period and, in order to avoid excessive boiling, the temperature must be reduced. All wet process cast iron enamels boil during firing, but towards the end of the operation the enamel quiets down and gives a smooth layer. The gases producing this boiling probably come mostly from the iron, although a considerable amount may be formed by the reaction at the inter-face of the iron and the enamel.

Dry Process Cast Iron Enamels. Dry process cast iron enamels are used on heavy castings and always require a ground coat. This ground coat is a viscous glass which does not readily decompose or give off volatile constituents. It fuses into the pores of the iron and produces a continuous thin layer of glass which prevents the iron from oxidizing and scaling. Since the castings are very heavy they are heated slowly, often in two steps. The preheating raises them to a temperature of a bright red heat and then they are transferred to the furnace at an enameling temperature of 1550 to 1700° F. As a casting reaches the temperature of the furnace, it is withdrawn and the cover enamel is dusted on the hot surfaces. It is then returned to the furnace until the enamel coating melts down to a smooth surface.

The ground coat (or grip coat) on dry process cast iron usually boils very violently in the first firing, which is probably due both to the gases evolved from the iron and the reactions at the inter-face.

It may be well to mention here the Manson effect,¹³ which is a test of the blistering characteristics of cast iron. If the cover enamel is dusted on hot iron, it boils violently in some cases and does not in others. Iron which undergoes this violent boiling gives an enamel of good adherence, while one which does not boil has poor adherence. This is evidence that good adherence and successful enameling are dependent upon the reactions between the enamel and the iron.

This discussion of firing shows that the chemistry and physics involved are very complicated and that the best efforts of the ceramist and chemist will be required before they are completely explained.

The Effect of Furnace Atmospheres. The furnace atmosphere in enameling furnaces is an important consideration and one which

¹³ E. P. Poste, *J. Am. Ceram. Soc.*, 16, 177-92 (1933).

usually comes to the enameler's attention, whether he wishes or not. There are three characteristic defects, which are sometimes caused by gassing, namely: iridescence, blistering, and scumming. Although these defects may be caused by the furnace atmosphere, they may also occur from other sources.

Blistering of enamels may be caused by the presence of water vapor in the furnace atmosphere. This water vapor may be present either from charging moist ware in the furnace or from the products of combustion of the fuel. Where the amount of moisture is not great the defect may take the form of a slight iridescence.

Iridescence is probably the most common defect caused by the atmosphere in an enameling furnace. It is also the least serious, and a slight iridescence is often neglected or allowed to go unnoticed.

The formation of a white scum on enameled ware after being fired is caused by the presence of sulphur. This sulphur may come from the enamel materials, the water, or the furnace atmosphere. It is easily recognized, since it has a salty taste. It can be washed off of the ware, but will usually re-form in a short time. It is chemically a combination of sodium, potassium, and calcium sulphates,* which when fused are immiscible with the enamel glass. It, therefore, floats to the surface during the firing operation. When cool it hydrates, taking up moisture from the air and producing the white scum.

Sulphur scum is sometimes formed by as low as .002 per cent sulphur oxide gases in the atmosphere of the furnace. It is possible for the atmospheres in congested industrial districts to contain this amount of sulphur dioxide; thus even an electric furnace is not proof against possible gassing. It must be remembered that even when the furnace gases do not contribute enough sulphur to cause trouble they may, with that added from the atmosphere of one of these congested districts, contain a detrimental amount.

In one case, the author's attention was called to a sample of enameled ware in which a yellow enamel design was fired over a black background, in an electric furnace. The black enamel had all the appearance of having been scummed by sulphur, as was actually the case. The yellow enamel was colored with a yellow stain, which contained cadmium sulphide. Some of this sulphur was driven off in firing the yellow enamel and it attacked the black background. On reversing the procedure and firing the yellow coat first, the difficulty was entirely

* An X-ray analysis of this material showed that it was not a simple sulphate, but probably one of complex nature.

eliminated, since the yellow enamel when once melted down ceased to give off sufficient sulphur to scum the black enamel. Many peculiar cases of gassing by sulphur are encountered, but, once the enameler becomes familiar with this defect, he will recognize it, as sulphur is different from all other types of scum.

In the firing of cobalt ground coat sheet iron enamels of the common type, it is necessary to have some atmospheric oxygen present in the furnace atmosphere, otherwise good adherence is not obtained and a ruffled appearance is produced. The fundamental reasons for this are not understood, but they are probably closely associated with the development of adherence. It is possible that enamels may be developed or conditions modified whereby it will be not only possible but desirable to fire enamels in atmospheres of low oxygen content. It is quite probable that, if such are developed and neutral atmospheres are used, the high grade enameling irons will no longer be necessary. Reducing or neutral conditions might thus inhibit the gassing of iron by preventing the oxidation of carbon and other impurities.

Some enamels are much more sensitive to gassing than others, but at the present time the information on this subject is quite limited. Dry process cast iron enamels are much less sensitive than sheet iron enamels and have actually been fired commercially in the products of combustion of coal gas. Many cast iron enamels are fired in furnaces where appreciable amounts of gases actually enter the firing chamber.

ENAMELING FURNACES

Box Type Furnaces. The enameling furnace has undergone many changes since the introduction of enameling in America, yet some of the furnaces used today have the same fundamental designs as those originally brought over from Germany.

Early Muffle Type. The early enameling furnaces were of the full muffle box type, constructed chiefly of fire clay refractories. The muffles were very thick, sometimes being built of standard fire brick, laid so that the heat from the combustion chamber had to pass through four and one-half inches of fire clay refractory. In the better furnaces fire clay slabs were used. These early furnaces were fired with coal in a combustion chamber under the hearth, the hot gases passing up around the walls of the muffle to a flue in the roof of the furnace. The front of the furnace was closed with a refractory door and the ware was charged and removed from the furnace by means of a large fork, suspended by a chain and tilted or swung into position by the operator.

FIGURE 85
FLOW SHEET FOR FIRING SHEET IRON ENAMELS

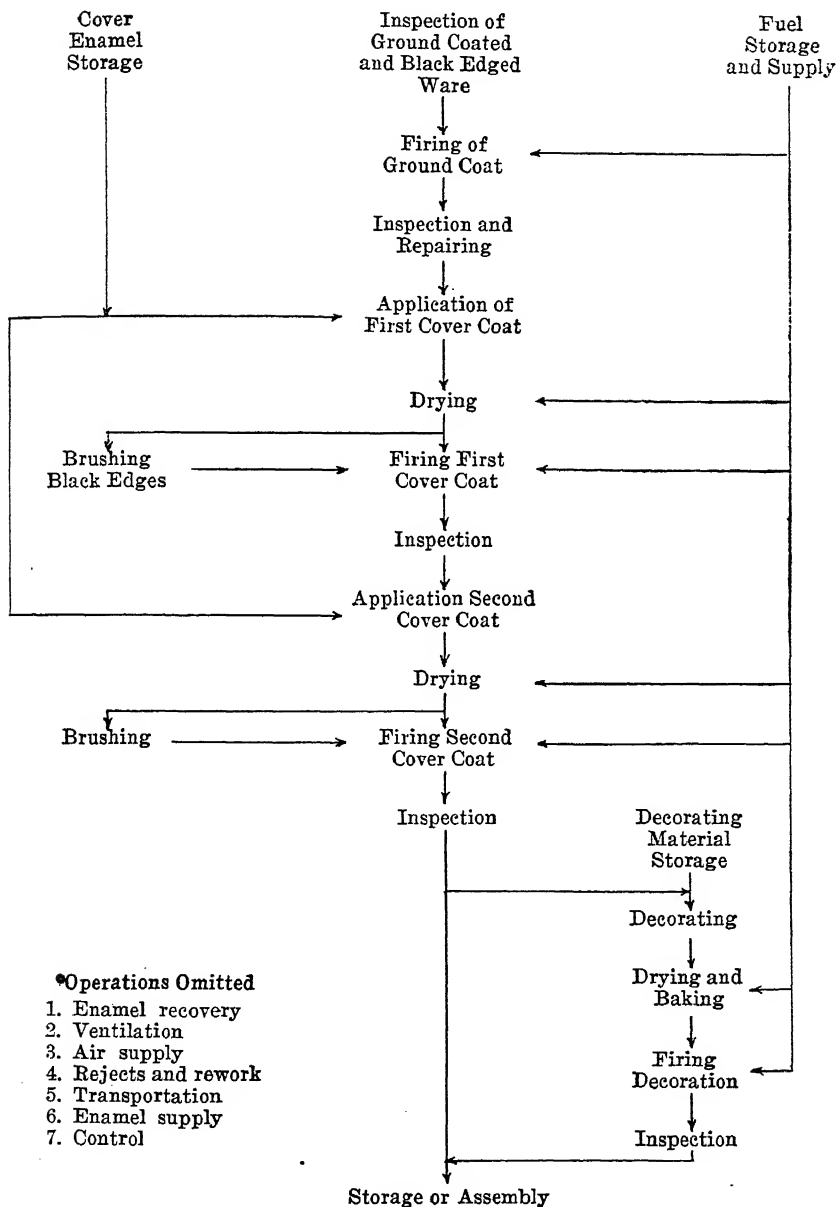
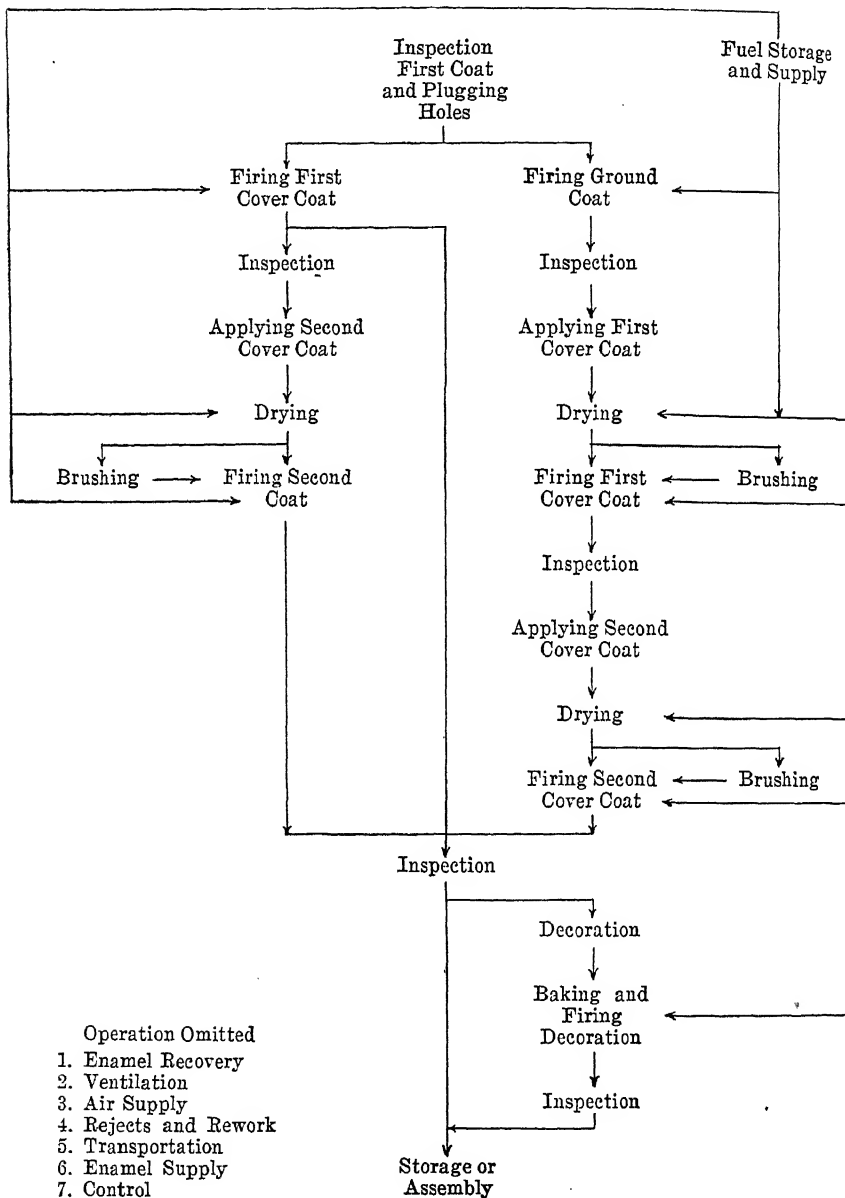


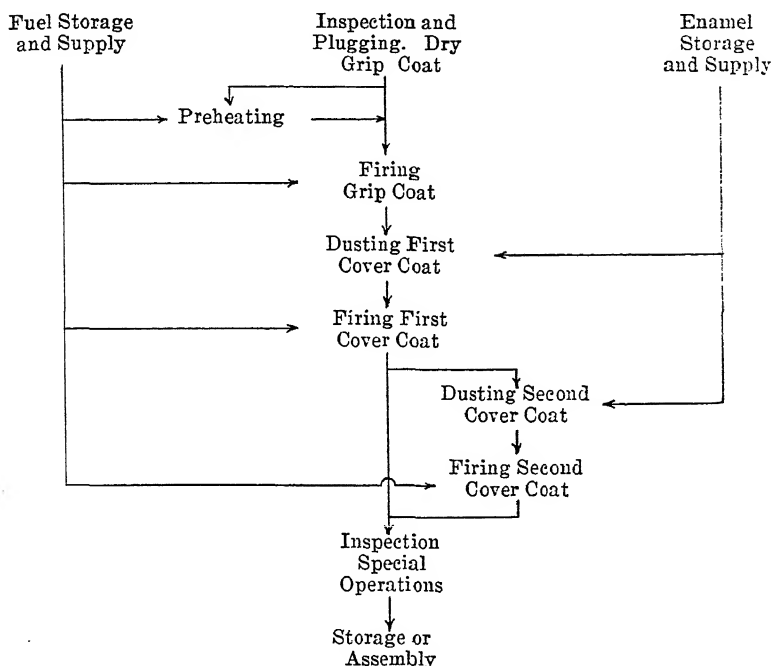
FIGURE 86
FLOW SHEET FOR FIRING WET PROCESS CAST IRON ENAMELS



The diagram shown in Figure 88 illustrates the construction of these muffle box type furnaces.

These muffle furnaces served very well in the early days when the production was low and coal was used as fuel, but with the introduction of oil and gas fuels many difficulties were encountered. The efficiency

FIGURE 87
FLOW SHEET FOR FIRING DRY PROCESS CAST IRON ENAMELS



Operations Omitted

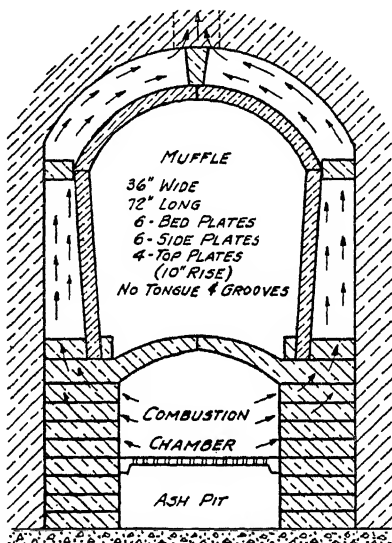
1. Enamel recovery
2. Rejects and rework
3. Transportation and Handling
4. Control

was low and the high temperatures produced by these new fuels caused the refractory clay muffles to fail. The products of combustion were no longer under a reduced pressure and they leaked through the muffles and damaged the ware.

Semi-Muffle Type. To improve the fuel efficiency of the furnaces, the semi-muffle type shown in Figure 89 was developed. In this furnace

the flame and products of combustion passed from the combustion chamber under the floor of the furnace up along the side walls and back of a muffle extending only a few feet from the floor of the furnace. The gases then followed the side walls and crown of the furnace to the flue located at the top of the crown.

This semi-muffle type of furnace had a lower upkeep and greater fuel efficiency than the full-muffle type, but the enamels were often affected by the combustion gases and the quality of the ware suffered.



FULL-MUFFLE BOX - TYPE GERMAN FURNACE
USED IN CONNECTICUT 1890

FIGURE 88.

Early Full-Muffle Box Type German Furnace.*

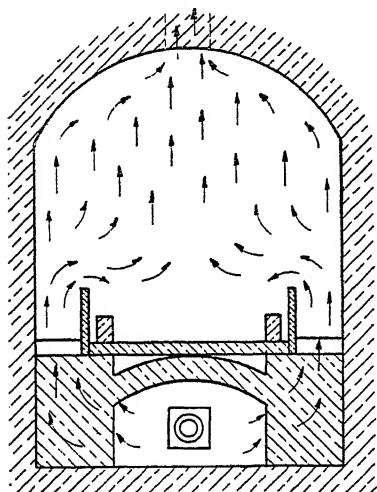
Intermittent Type. The intermittent type furnace was designed to eliminate the difficulties from the gases of the semi-muffle type and to retain the increased fuel efficiency.

No muffle was used in the intermittent type furnace, the gas or oil being fired in the enameling chamber. When the furnace walls had absorbed enough heat and the desired temperature was reached, the burners were shut off and the ware charged into the furnace through the door. As the door opened, any residual gases from the fuel rushed up the stack. The door was then closed and the enamel ware was fired from the residual heat in the walls of the furnace. On removing the

* F. S. Markert, Thesis, University of Illinois (1933).

ware from the furnace the cycle of operations was again started, the burners being turned on for another heat.

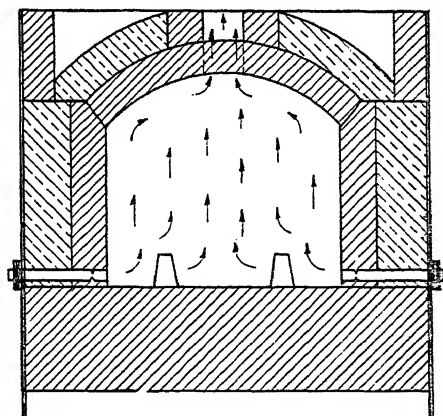
This type of furnace was quite successful and a few of them are still in use. When these furnaces were designed the time lost during the heating operation was utilized in charging the fork for the next burn, but when the speed forks were introduced this loss of time became more objectionable, because the added rate of production could not be utilized. Another frequent objection to the intermittent type of



SEMI-MUFFLE BOX-TYPE
GAS OR OIL FUEL

(a)

FIGURE 89.
Semi-Muffle Box Type.†



INTERMITTENT-BOX-TYPE
GAS OR OIL FUEL

(b)

FIGURE 90.
Intermittent-Fired Box Type.*

furnace is that the ware is fired over a period of decreasing temperatures. It is charged to the furnace at a high temperature and the firing is finished at a low temperature. This is not objectionable for light weight stock, such as kitchen ware, but with heavier gauge iron the enamel melts before the iron comes up to temperature. This may be objectionable, since uniform heating is the desired condition in all enamel firing. Figure 90 shows the general design of the intermittent type furnace.

Modern Muffle Type. With the improvement of muffle refractories the full-muffle type of furnace again gained popularity. These refrac-

† *Ibid* 1.

** *Ibid* 2.

tories were made of silicon carbide and fused alumina, which, with their strength at high temperatures and their good thermal conductivity, added greatly to the efficiency of the muffle furnace. The shapes could be made as tiles with tongue-and-groove joints, so that the muffle was not only thin, but much tighter than those previously used. The new furnaces were designed for the fuel to be used and were much more efficient than the older types. Various schemes were used to increase the radiating surface of the muffle and automatic temperature control was introduced. The charging apparatus was improved so that the furnace could be utilized to capacity.

A modern box type muffle furnace is shown in Figure 91. It is fired by burners in the back and under the hearth. The gases rise around the muffle and pass through the heat reclaimer to the stack. This furnace is built with the V-type Manion hearth, which greatly increases the radiating surface. The muffle is constructed of alundum tile and the floors are built up of alundum brick. Kaolin brick are used for the support of the ware and the muffle. The chamber around the muffle is lined with fire clay brick, backed up with insulating brick. Common brick are used for the outside walls, and I-beams act as buck stays to retain the shape of the furnace. When this type of furnace is fired with oil, one burner may be sufficient, but when fired with gas, as many as a dozen burners may be used.

Markert¹⁵ states that the average fuel consumption of this furnace, operating at 1540-1580° F, is sixteen to eighteen gallons of oil, 2600-3000 cubic feet of artificial gas (550 BTU), or 1300-1500 cubic feet of natural gas (1050 BTU) per hour and that the capacity is twelve loads of ware per hour, or an average of 600 square feet of eighteen or twenty gauge ware.

Another modern box type muffle furnace used for wet process enamels is shown in Figure 92. This furnace is similar to the one described in Figure 91, except that it has the conventionally shaped muffle of silicon carbide and a heat reclaimer. Typical muffle sizes are shown in Table 43.

TABLE 43
MUFFLE SIZES

<i>Height</i>	<i>Width</i>	<i>Depth</i>
24-36"	48"	12'
24-36"	54"	12'
24-36"	60"	12'

¹⁵ F. S. Markert, *The Development of a Continuous Enameling Furnace*, Thesis, University of Illinois (1933).

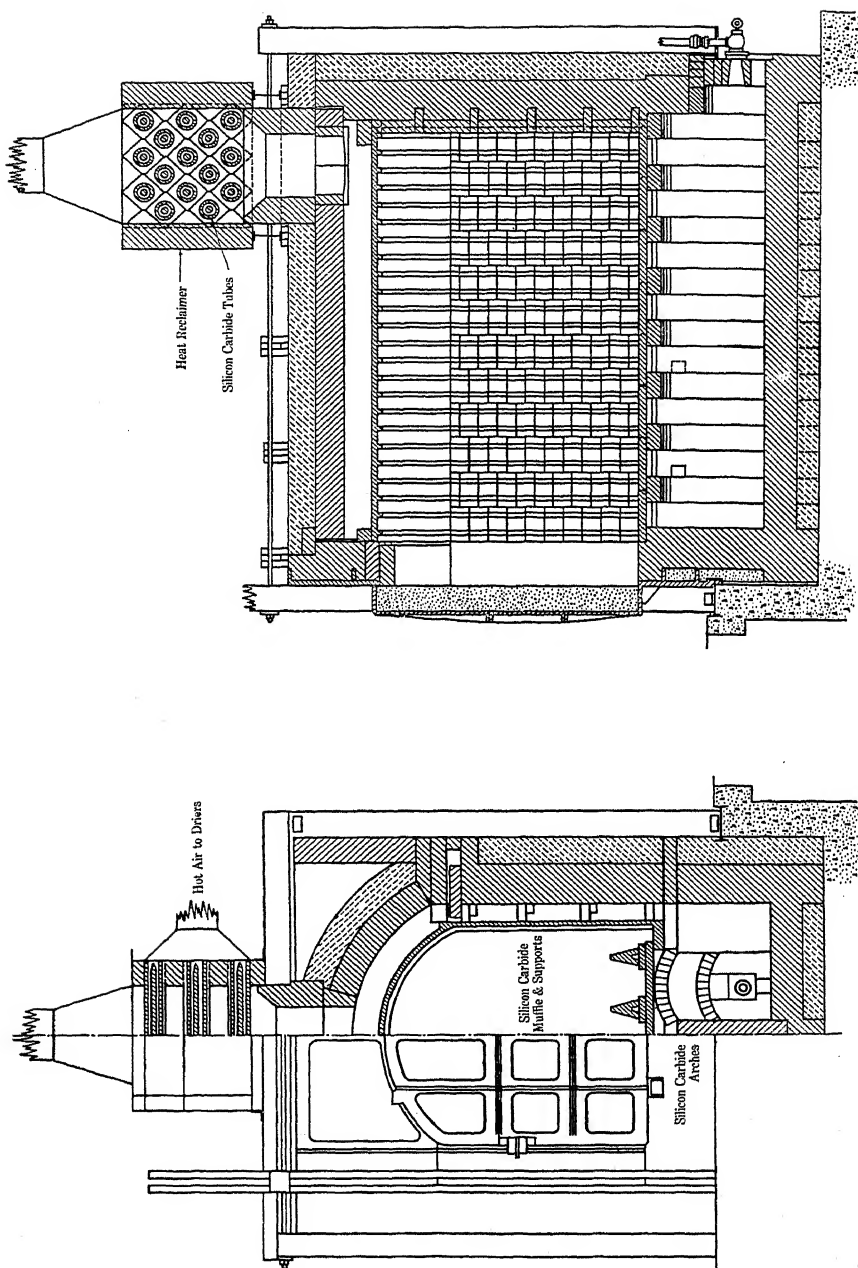


FIGURE 92. Modern Muffle Type with Heat Reclaimer.

Silicon carbide has a very high thermal conductivity, which greatly improves the efficiency of this furnace over the fire clay type. The drop in temperature between the combustion chamber and the inside of the muffle is not so great with the silicon carbide; therefore the temperature in the combustion chamber need not be carried so high. This decreases the cost of fuel and prolongs the life of the refractories.

The floating-flue type of muffle furnace is shown in Figure 93. This furnace represents a method of greatly increasing the radiating surface of the muffle. The gases from the combustion chamber enter the floor of the muffle, pass up and around the firing chamber through tubes to a collecting flue in the roof, and thence to the stack. Since these hollow tubes are thin walled and made of refractories having good thermal conductivity, the heat from the gases is readily transferred to the firing chamber of the furnace.

A modern sanitary ware furnace is shown in Figure 94. This furnace is designed for dry process enameling with a large, well supported floor of silicon carbide and a muffle on each side. It also has a recuperator to conserve the heat carried out of the furnace with the flue gases.

An electric box type furnace is shown in Figure 95. The resistance elements in this furnace are placed in the roof and the floor, although in many designs they are located on the side walls, back, and door of the furnace. The elements are a nickel chromium alloy and are

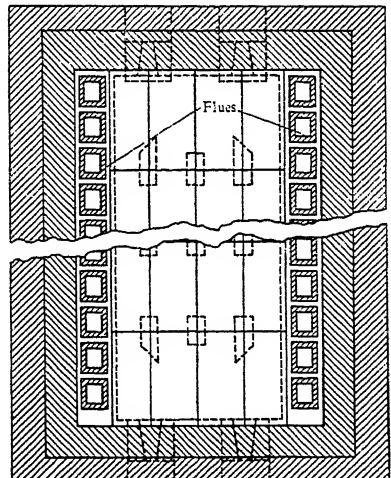
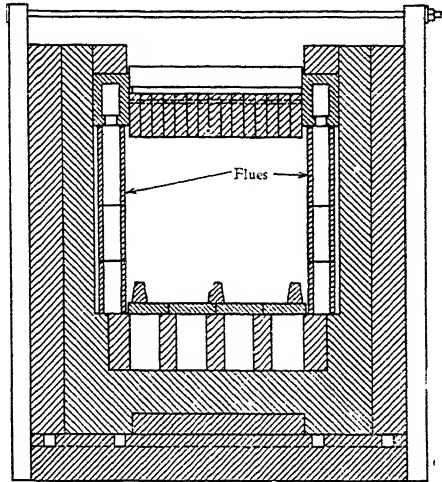


FIGURE 93.
Floating Flue Type.

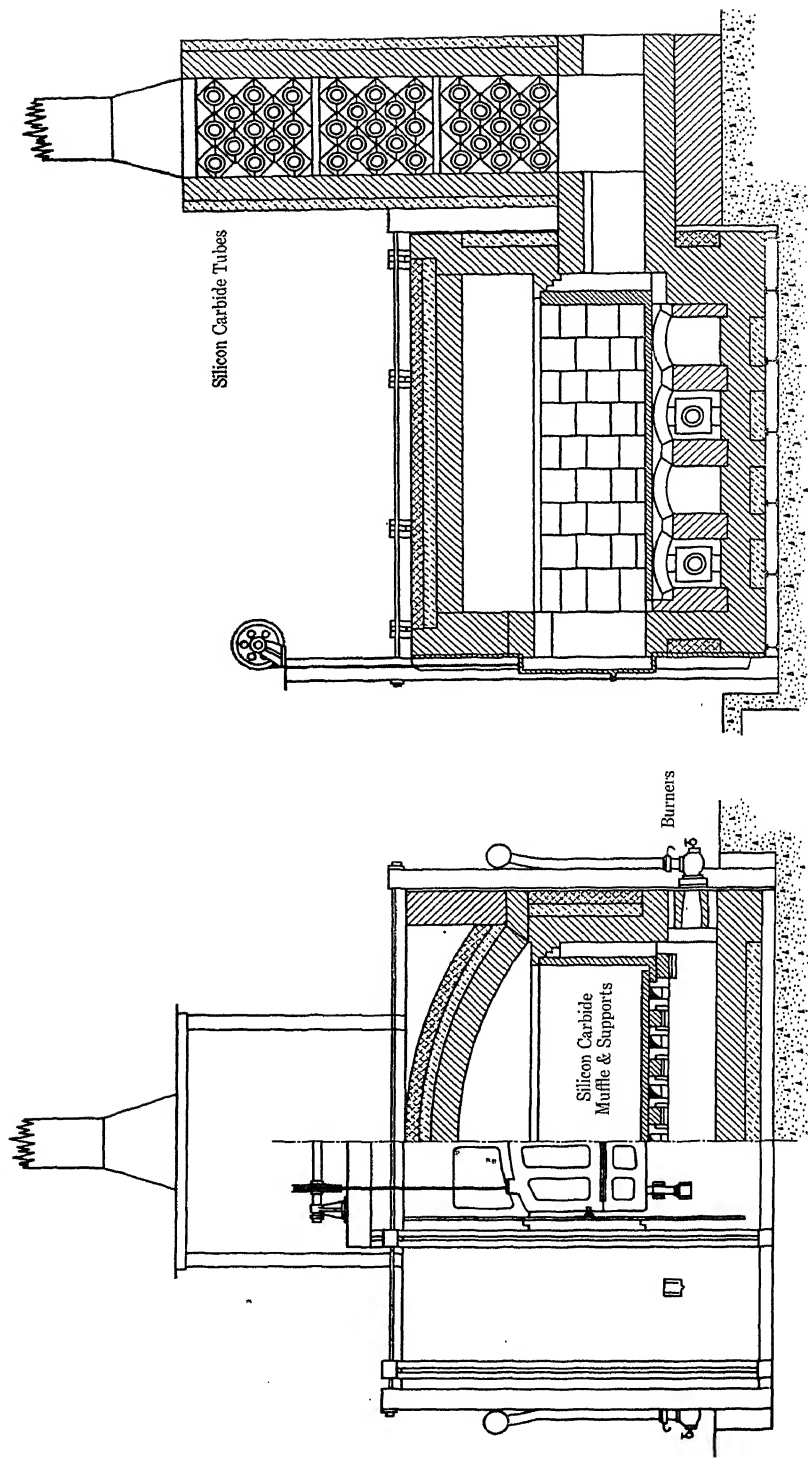


FIGURE 94. Modern Sanitary Ware Furnace.

satisfactory for temperatures up to 1800° F. The advantage of the electric furnace is the absence of combustion gases and the elimination of the muffle.

CONTINUOUS ENAMELING FURNACES

Although the intermittent batch type furnace has been developed to a greatly improved efficiency, certain fundamental faults cannot be overcome. It does not fit in well with continuous production, where the ware moves from one operation to another without interruption. It

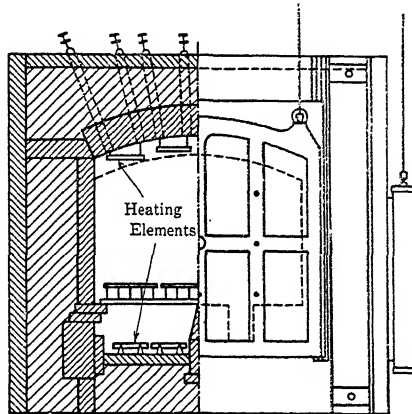


FIGURE 95.
Electric Box Type Furnace.

also has the disadvantage of not reclaiming the heat lost in the cooling of the ware. The enamel enters a hot furnace and leaves a hot furnace very suddenly, which is not in accord with the principles for attaining uniform heating and cooling. The development of a continuous enameling furnace has been, therefore, a natural result. Early attempts in this direction met with many failures before they were successful, but each attempt was encouraging and now the modern continuous furnace is rapidly replacing a great many of the intermittent type.

Circular Enameling Furnace. The first successful continuous furnaces were of a semi-automatic type, being circular and charged and discharged by hand. A single opening was used for both charging and discharging the ware, which was fired as it passed around the circular path through the hot furnace and back to the opening. Two types of conveyors were used, the platform and the overhead types. It was

about this time that the electrical resistor elements came into common use, making it possible to heat these furnaces electrically. The burning tools on both the platform and overhead conveyors were made of the heat resisting alloys, thus reducing the weight and the accompanying loss of heat. The overhead conveyor consisted of a large iron wheel with rods hanging from the circumference through a slot in the top of the furnace. The ware was hung on these rods. This circular type of semi-continuous furnace is shown in Figure 96.

These furnaces were successful for certain types of ware and a few of them are still in operation. They did not, however, meet the diversi-

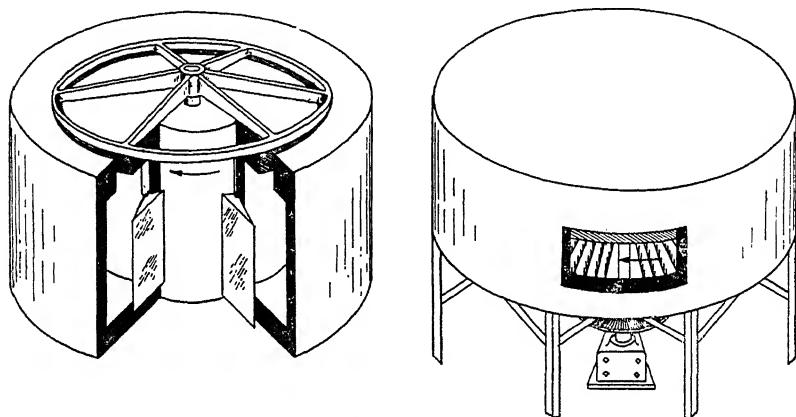


FIGURE 96.

Circular Slotted-Roof Type and Circular Hearth-Conveyor Type.*

fied demands of the industry. They subjected the workers to considerable heat and the capacities were comparatively small. They were not adapted to gas or oil fuel and the labor required showed little saving over the intermittent type of furnace.

Tunnel Furnace. The first successful, really continuous enameling furnace was put into operation in 1924. It was a straight line furnace built with two tunnels side by side, which were 135 feet long and divided into a heating zone, a 26-foot firing zone in the center, and a cooling zone. The ware was conveyed through the furnace by an overhead continuous conveyor traveling $9\frac{1}{2}$ feet per minute. This conveyor was mounted on sprockets at the ends of the furnace, which provided the turn so that the movement was in one direction in one tunnel and in the opposite direction in the other. This permitted the cooling ware on one side to warm the heating ware on the other. The conveyor

* F. S. Markert, Thesis, University of Illinois (1933).

proper was hung above the furnace and from this, rods extended down through a slot in the top of the furnace, supporting the burning (firing) racks. The conveyor extended sixteen feet beyond the brickwork at one end and thirty-six feet beyond it at the other. This gave ample space for loading and unloading the ware. In the plant where this furnace was first installed, twenty-five per cent less floor area was required than formerly. The labor was reduced by one-half and the fuel cost by one-third.¹⁶

An oil-heated muffle in the bottom supplied 85 per cent of the heat and electric resistance elements along the side walls furnished the remainder. These electric elements were controlled automatically so that the temperature of the furnace could be kept constant.

The production of this furnace was very satisfactory, kitchen ware of twenty-four to twenty-eight gauge being fired together. The production was 500,000 pieces of two- and three-coat ware per month. Later this furnace was changed to gas fuel and the electric elements were eliminated. The gas was put under automatic control.

Designs for Continuous Furnaces. Following the success of this furnace the continuous enameling furnace developed rapidly and many new designs and modifications came into existence. The diagrams in Figure 97 show some of the designs brought into use. Furnaces (a), (c), and (h) are the most common and generally accepted designs.

The original type of furnace is represented by (a), (b) being a modification of it with only one tunnel. This furnace has several disadvantages which are difficult to overcome. Since it is a straight-through furnace with the hot zone in the middle, there is a strong tendency for air currents to pass through the furnace and reduce the efficiency. This can be largely overcome by the use of the air screen, which was soon introduced. Another disadvantage of this furnace is its length, which makes it difficult to fit into most shops. The floor space required is large and the fact that the ware charges and discharges from the two ends makes supervision difficult.

The U or hairpin type of continuous furnace (c) was designed to eliminate these faults and, so far as space is concerned, it is a decided improvement. Heat loss through the doors was, however, still an important consideration and the air screen was used. Types (d), (e), and (f) were designed to improve this and to eliminate the congestion of the ware in the hot zone at the turn. In the U-type of furnace

¹⁶ Robert McDougal, Continuous Furnace Enamels, 500,000 Pieces Per Month, Ceramic Industry VIII, 209 (1927).

space must be left between tools to permit the turn without wrecking the ware.

The incline furnace (h) was designed to pocket or trap the hot zone at a high point in the furnace, thereby preventing air currents

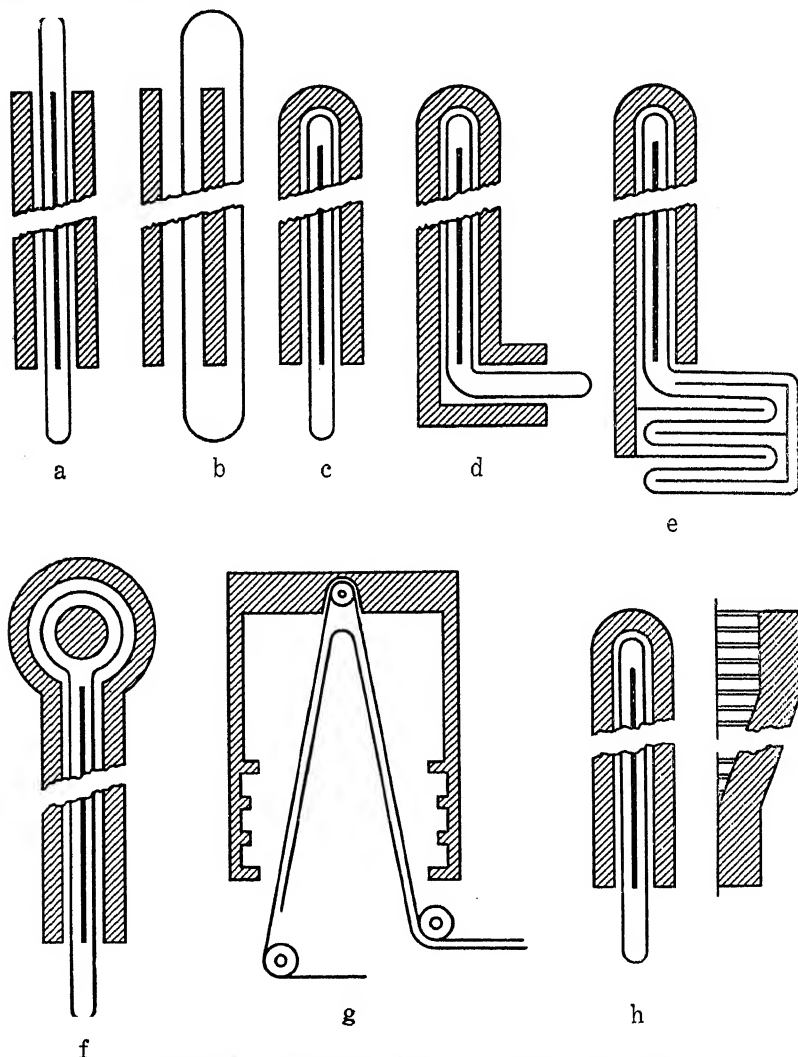


FIGURE 97. Designs for Modern Continuous Furnaces.

passing through the furnace. This improved the operation but the air screens at the doors of the furnace are used for further conserving the heat.

The vertical furnace (g) was designed with the same purpose in mind as the incline furnace, *viz.*, to trap the hot air. Since hot gases rise, it was believed that the circulation in and out of such a furnace would be at a minimum. This furnace, however, must have hanging tools so that the ware can pass from an upward to a downward direction. This brings about a new difficulty, namely: the top of each piece of ware enters the furnace first and leaves last, therefore, it receives a harder firing than the bottom. For ware of small size or ware fired in a horizontal position this difficulty is not important, but clearance at the change of direction limits the size and amount of ware.

The design of the muffle, the proportions of the furnace, and the general construction represent much of the progress in continuous furnace development. It is through the combined efforts of the enameler and the furnace engineer that great progress has been accomplished.

All continuous enameling furnaces can be divided into the firing chamber, the preheating, and the cooling zone. The firing chamber must be of a muffle type, if either gas or oil is employed, but may be direct fired, if electric resistance units are used. The latter offers the simpler problems of construction, since the temperatures nowhere exceed 1800° F and the muffle construction is entirely eliminated. Heat distribution is a matter of proper distribution of the resistor elements and there is an automatic off-and-on control. Combustion gases are not encountered and the usual gases which may collect in the furnace escape through the conveyor openings in the crown.

The gas- or oil-fired furnaces may have temperatures of 2200°-2300° F in the combustion chamber when the firing chamber within the muffle is no higher than 1600° F. This introduces added problems in the choice of refractories and proper construction. Since the products of combustion from gas or oil must not enter the firing chamber, a tight muffle and proper design of flues and combustion chambers is necessary.

In the early furnaces the fuel was fired in one large chamber under the floor of the muffle, but in the more modern types the V-bottom and the multiple combustion chambers are being used. The multiple transverse combustion chambers are used in the U-type furnace, the alternate chambers being fired from opposite sides and the products of combustion passing up the sides of the furnaces back of muffles to tunnels under the floor of the preheating chamber. The gases are then drawn off to the stack. The muffles are constructed of alundum or silicon carbide to give resistance to high temperatures and high thermal conductivity. Automatic burner control and sometimes automatic

stack draft control are used on these furnaces. Pre-mix gas burners are usually employed to give complete combustion, and where fuel oil is used the oil and air pressures should be controlled. Secondary air may be admitted in the latter case, but in the former all the air needed enters the pre-mix chamber. A typical oil installation will use air at sixteen ounce pressure and the fuel oil at about twenty pounds and both are supplied to the several burners from a single pressure source.

The length of the firing chamber varies with the desired production of the furnace. With a long firing chamber, the enamel is properly fired with a fast moving conveyor chain, which results in large pro-

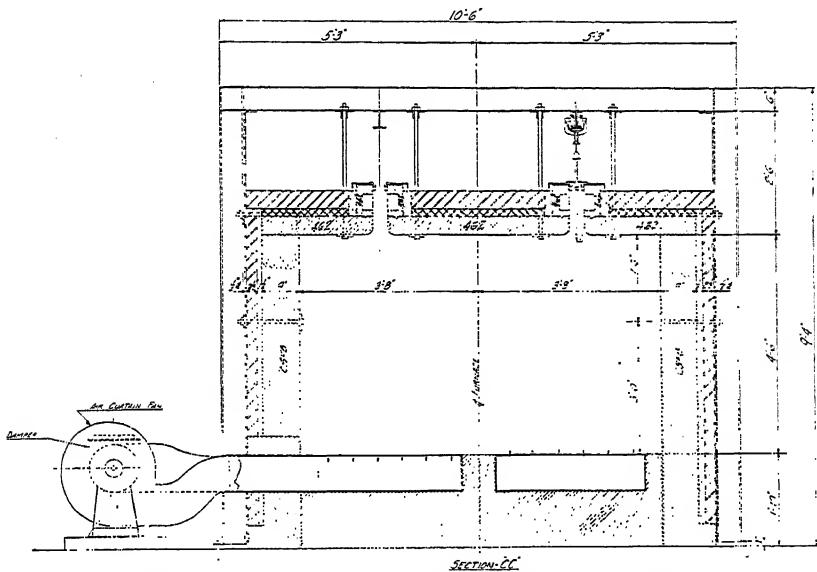


FIGURE 99. The Air Curtain in a Continuous Furnace.*

duction. If the firing chamber is short, the conveyor (and production) must be slowed down; otherwise the ware will not remain long enough at the firing temperature to fuse the enamel properly.

The preheating and cooling chambers also vary in length from 40 to 80 feet. The longer zone gives increased economy of fuel and furnace efficiency, but the shorter zone does not take as much floor space in the enameling shops. An air curtain, Figure 99, is often used in this zone of the furnace to aid in the transfer of the heat from the cooling to the preheating ware. It usually consists of a motor-driven, large capacity blower, which draws the heated air down into a chamber under the hot

* *Ibid.*

head continuous chain, but in a few cases the floor conveyor is used, as shown in the diagram of the enameling furnace in Figure 102.

This latter type of conveyor must necessarily contain more weight than the overhead conveyor, but in some cases the saving in tooling weight compensates for this.

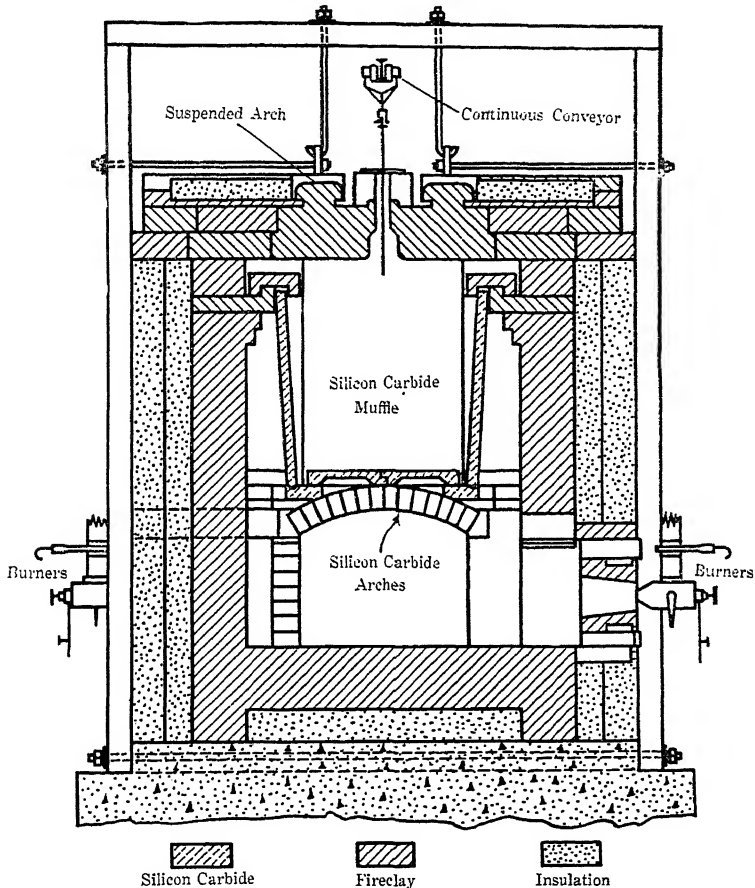


FIGURE 101.

A Section Through the Firing Zone of a Continuous Furnace.

The overhead conveyor is generally supported by a steel frame and is built outside of the furnace, rods extending to the interior through a three-inch slot in the roof of the furnace. The tools supporting the ware are hung on these vertical rods. Sometimes a hood is built over the conveyor to prevent a draft from the interior of the furnace

passing through the slot. In the preheating and cooling zones this hood is tight, but in the hot zone a small amount of air is allowed to escape, to ventilate the furnace and to prevent the concentration of the heat at the conveyor. The objections to the overhead conveyor are the danger of falling dirt and the construction difficulties. In some installations,

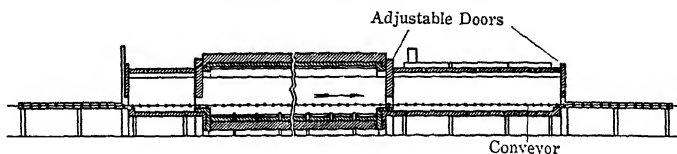


FIGURE 102. The Floor-Conveyor Type Furnace.

the conveyor passes through a brush and air cleaner after each passage through the furnace.

The metal parts within the furnace are made of heat-resisting alloys, such as those shown in Table 44.

TABLE 44
ALLOY ANALYSES (MARKERT)

	<i>Cast</i>	<i>Rolled</i>	<i>Drawn</i>
Nickel.....	30-34	30-34	80
Chromium.....	18-22	18-22	20
Manganese.....	2.5-3.5	2.5-3.5	trace
Silicon.....	1.5-2.5	1.0 max.	trace
Carbon.....	.4 max.	.4 max.	trace
Iron.....	balance	balance	trace

An alloy, to be suitable, must withstand the heat, must not oxidize or scale excessively, must be strong at the temperatures of the furnace, and must withstand repeated heating and cooling.

The tools are made as light as possible in order to reduce the amount of heat loss. Where intricate shapes are used the cast alloy is more suitable, because it avoids the necessity of welds, which are difficult to make and have a tendency to crack and warp. The drawn wire is common for hooks and braces.

The production of enamel ware in a continuous furnace depends upon a great many factors and is difficult to predict or even approximate. The total quantity to be produced and the uniformity from hour to hour, day to day, and even season to season affects the production figures. The variety of ware, such as sheet iron or cast iron, the

TABLE 45

CONTINUOUS FURNACE PRODUCTION

No.	Furnace	Combustion Chamber	Fuel and RTU	Fuel Consumption per hour Cu. ft. or Gal.	Production		Cham. Speed ft. per Minute	Temp. ° F.	Enamel	Ware
					Sq. ft. per hour	Pounds per hour				
1	U-type	9-burner	Gas	7100 cu. ft.	5000	7500	17	1560	Final Coat	Sheet Iron
2	U-type	9-burner	Gas	4200-4500	5000 pieces	3750	18-20			Hollow Ware
3	U-type	7-burner	Oil 144,000	32		7870	9.4	1580	Ground	Refrigerator Linings
4	U-type	7-burner	Oil 144,000	30		7870	9.4	1510	1st White	Refrigerator Linings
5	U-type	7-burner	Oil 144,000	31		7870	9.4	1530	2nd White	Refrigerator Linings
6	U-type	7-burner	Gas 1050	3600	2400		8	1580	Ground	Stove and Heater Parts
7	U-type	7-burner	Gas 1050	3200	3600		12	1540	Cover Coat	
8	Straight through		Gas	6180	826	1104		1610	Ground	12-24 Gauge
9	Straight through		Gas	6500	1482	1962		1560	1st and 2nd Cover	12-24 Gauge

1-7. F. S. Markert, Thesis, Ceramic Dept., University of Illinois, Urbana, Illinois (1933).

8-9. Ceramic Industry, 285 (1930).

shapes, and the amount of tooling necessary affect the production. The enamel characteristics, the number of coats, the amount of decoration, and the efficiency of the plant operation must be considered. Such varying conditions make every installation of a furnace an individual problem.

The production figures presented in Table 45 are, therefore, approximations representing certain set conditions. They give some idea of the production of continuous furnaces, however, and are presented for this purpose.

Figure 98 shows a plan view and a longitudinal section of a continuous fuel-fired U-type furnace, and Figure 101 shows a vertical section through the firing zone in a tunnel type continuous furnace. Figure 102 shows a furnace in which the conveyor is on the floor of the furnace, thus eliminating tool weight, but adding to the conveyor weight.

Note: In appreciation the author wishes to acknowledge the co-operation of The Carborundum Co. and The Ferro Enamel Corp. in furnishing certain of the furnace diagrams contained in this chapter

CHAPTER 12

Enamel Properties and Tests

Although enamels have reached a state of wide application, the tests used to determine their properties have not been generally standardized. This is probably the case because the varied uses, to which enamels are put, subject them to different requirements. It is not possible to obtain the highest excellence of all properties in one enamel; therefore certain properties are sacrificed to permit the improvement of others, which for some particular use are more important. Thus, the high first gloss or the fusibility may be sacrificed in some degree to improve the acid resistance. Acid resistance may be sacrificed for alkali resistance and vice versa.

THERMAL PROPERTIES

The properties of enamels related to temperature or temperature changes are (a) fusibility and fluidity, (b) thermal expansion and contraction, (c) resistance to thermal shock, (d) thermal conductivity, and (e) miscellaneous properties, such as specific heat, radiation, reflection, and surface tension. The fusibility of enamels and the fluidity in the molten state are of primary importance in the smelting and firing of enamels. The other properties are important in both the processing and the finished ware.

FUSIBILITY AND FLUIDITY

The fusibility and fluidity of enamels are essentially controlled by the compositions. However, the compositions of enamels are so complicated, that any method for calculating the fluidity or fusibility, theoretically, will be either very complicated or empirical. Many attempts have been made to discover satisfactory factors for calculating the fusibilities of glasses. Some of the proposed formulæ have been applied to enamels, but the results are of limited value, and are applicable only to glasses lying within a narrow range of composition. However, some of these factors show considerable promise in the calculation of the fusibilities of enamels.

Staley,¹ in a series of articles extending over a number of years, has developed a set of factors for calculating the fusibility of enamels. In their most recent form they are as shown in Table 46. These factors

¹ U. S. Bur. Std. Tech. Paper, No. 142 (1919); *Ceramist* 6, 384 (1925); M. E. Manson, A. P. Woolfolk, R. C. Boyd, A. Malinovsky, and H. F. Staley, *Ceramist* 8, 38 (1926).

² R. R. Danielson and Tetrick, Viscosity and Reboiling of Blue Ground Coats, Presented at the Meeting of the Am. Ceram. Soc., February (1934).

The results of the calculation for five sheet iron ground coats and a comparison with the results of the fusion block test are shown in Table 47. A close relationship is indicated.

TABLE 47
COMPARISON OF THE REFRACTORY INDEX WITH RESULTS FROM
THE FUSION BLOCK TEST

<i>Enamel</i>	<i>Refractory Index</i>	<i>Fusion Block Flow in Notches</i>
A	0.74	6+
B	0.87	5
C	0.96	4+
D	1.06	3
E	1.13	2

The fusibility of sheet iron ground coats, determined experimentally by means of the interferometer, is shown in Figure 103.

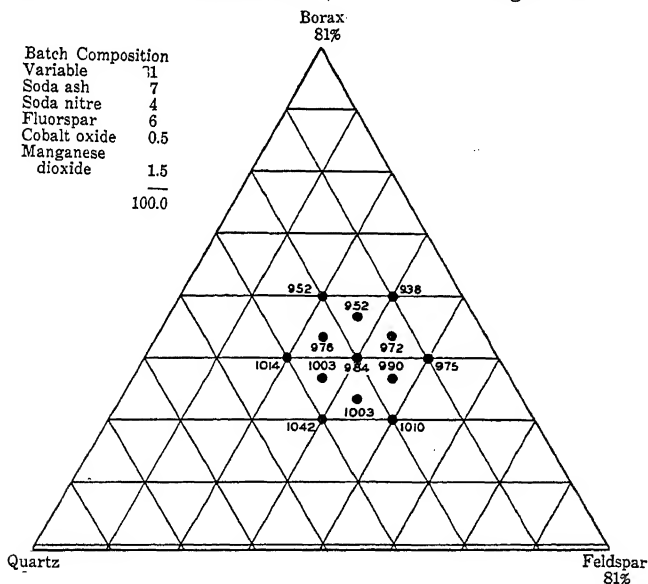


FIGURE 103.

The Fusibility of Sheet Iron Ground Coats in Degrees Fahrenheit.

These data show that an increase in the borax content of the batch produces a decided lowering of the softening temperature, an increase in the quartz content of the batch produces a decided increase in the softening temperature, while feldspar has little effect on the softening temperature of the sheet iron ground coat when substituted for borax and quartz. To convert these values to factors would, however, be

misleading, as they are not applicable quantitatively to other types of enamels.

The effect of the fluorides on the fusibility of sheet iron cover enamels as indicated by the interferometer test is shown in Figure 104.

With the exception of the method of maximum heat absorption, all of the tests for the fusibility of enamels involve the property of fluidity. The enamel glass gradually loses its rigidity on heating and

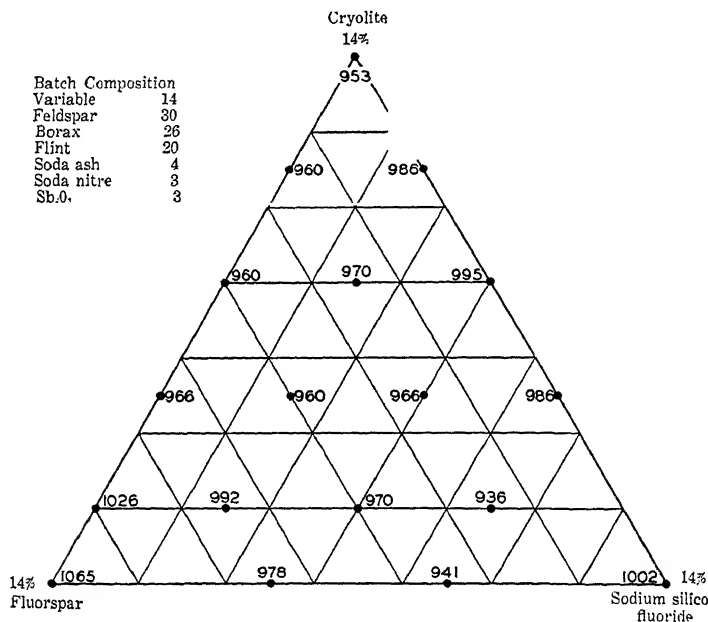


FIGURE 104.

The Effect of Fluorides on the Fusibility of Sheet Iron Cover Enamels (Degrees Fahrenheit).

softens until it flows. If the enamel melt is mobile, the fusion point is quite abrupt, but if it remains viscous, it is gradual and difficult to detect.

The cone fusion test, the button test, the fusion block test, the interferometer test, and the test for maximum heat absorption are the most satisfactory for determining the fusion points of enamels. These tests are all more or less empirical, but they give relative fusion temperatures, which are of value in the comparison of different enamels.

The Cone Fusion Test. The standard method³ for the cone fusion test, as adopted by the American Ceramic Society, is as follows:

³ The Standards Report of The Am. Ceram. Soc., J. Am. Ceram. Soc. 11, 465 (1928).

This method is applicable to frits and milled enamel.

(1) **Preparation of Sample.** A representative sample of frit or milled enamel should be thoroughly dried and ground in a porcelain pebble mill to pass a Number 150-mesh sieve.

(2) **Test Pieces.** The test pieces should be the size and shape of pyrometric cones, tetrahedra $\frac{5}{8}$ inch along the edge of the base and $2\frac{1}{2}$ inches high. They should be molded from a mixture of the powdered enamel and water with enough organic binder to produce the necessary plasticity and cohesion. The test pieces should be thoroughly dried upon removal from the molds.

(3) **Mounting.** The test pieces should be mounted on a plaque of asbestos board or strip of steel which has been coated with enamel. The base of the test pieces should be embedded in a plastic mixture such as sand, clay, and water, and their troweled faces should make an angle of 82° with the plaque. One or two pairs of test pieces from one or two enamels should be placed on a given plaque in the manner shown in Figure 105, permitting the end of the thermocouple to be equidistant from the tips of each pair of test pieces without being touched thereby during deformation. The mounting should be thoroughly dried before being placed in the furnace.

(4) **Furnace.** The furnace should be one which will give a definitely oxidizing atmosphere. It should be subject to accurate temperature control through the range 800 to 1600° F. It should be equipped with a pyrometer, the thermocouple of which should terminate near the center of the horizontal plane of the furnace and one inch or farther below the top. The pyrometer should be of such type as to afford an accuracy of $\pm 10^\circ$ F, with proper corrections for cold end temperature.

(5) **Placing of Test Pieces in Furnace.** The mounting should be placed in the furnace in such a manner that the tips of the test pieces from each enamel are $\frac{1}{2}$ inch above the center of the thermocouple and horizontally equidistant therefrom.

(6) **Rate of Heating.** The furnace should be at or below 800° F when the test pieces are placed therein. The rate of heating should be the following:

Start.....	800° F
10 minutes.....	1020
20 minutes.....	1150
30 minutes.....	1260
40 minutes.....	1370

(7) **Observation.** The "starting time" should be the instant that the pyrometer indicates a temperature of 800° F on recovering from the drop in temperature caused by the introduction of the test pieces. Each test piece should be observed separately with reference to the temperature of initial bending of the tip and final bending of the tip to the level of the base. The first observations should be averaged as the "starting temperature" and the final as the "deformation temperature." The difference between the two should be taken as the "deformation range." Two or more closely checking runs should be averaged for final results.

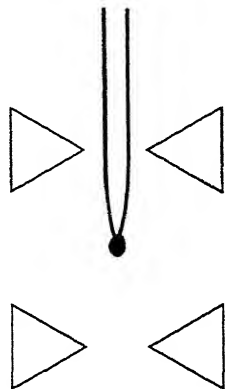


FIGURE 105.
Cone Fusion Test.

A. B. C. *Degrees F.* This test was adopted by the Enamel Division of the American Ceramic Society ⁴ in February, 1930.

1640 **The "Button" Cylinder Test.**⁵ This method consists of heating pellets of the enamel glass on a panel placed horizontally for a sufficient period of time to cause a softening of the glass, and then by means of a suitable device, alter the panel to a vertical position, with the result that the enamel flows down the vertical surface.

1600
1560
1520
1480
1440

For this method the number 60- to 80-mesh enamel is made into cylindrical pellets $\frac{1}{2}$ inch in diameter and 1 inch high. They are then placed on a panel in a horizontal position in the furnace and heated for three minutes, when the panel is lowered to a vertical position. It is left in this position for ten minutes and then removed from the furnace.

1400
1360
1320

Figure 106⁵ shows the results for three white cover enamels on a plate coated with ground coat enamel. It is evident from these results that A and B are more viscous than C. In some cases the enamel blisters at the high temperatures. Some enamels spread over the ground coat and others form a narrow stream. It is likely that surface tension and fluidity are as important as fusibility in this test, but the value of the test lies in the comparison of different enamels on the basis of these properties.

1280
1240
1200

A modification of this test, used at the National Bureau of Standards, gives numerical values for the fusion. In this test moistened frit was pressed into cylinders $\frac{3}{4}$ inch in diameter and $\frac{3}{4}$ inch tall. These cylinders were placed on a plaque and heated at a definite temperature schedule. As the temperature approaches the fusion point of the enamels they gradually slump down to the shape of a button. The end point

FIGURE 106.
Button Cylinder Test.

⁴ Bul. Am. Ceram. Soc., 9, 269 (1930).

⁵ C. J. Kinzie, Method for the Study of the Relative Viscosity of Enamel Glasses. J. Am. Ceram. Soc., 15, 357 (1932).

was taken as the temperature at which the slumping down reached a certain height.

The results of this test are definite values, reproducible and readily interpreted.

The Fusion Block Test. The fusion block is a porcelain shape, such as is illustrated in Figure 107.

The enamel powder is moistened and packed into the space above the incline, and allowed to dry. The block is then placed in the furnace at 600°C and heated 3° per minute. The enamel sinters, softens, and then starts to flow down the incline surface. The temperatures are taken at the start of flow and at the time the enamel stream passes each intersection on the incline. The temperature at which the enamel reaches the lowest intersection is usually taken as the fusion temperature.

The Bead Test. In the bead test small chips of enamel (not over one millimeter in diameter) are placed on the flattened end of a thermocouple in a small, electric, tube furnace. A telescope is placed at one end of the tube, and a light at the other. As the temperature increases in the furnace, the small chip of glass first rounds off at the corners, then forms a globule and finally slumps down. The temperatures at these three points can be taken together as a measure of the fusibility, fluidity, and surface tension phenomena.

This test has been used to some extent for the control of frits, but when different compositions are tested the behaviors can not be readily compared and interpreted.

The Interferometer Test. In determining the coefficient of expansion of glasses by means of the interferometer, the expansion curve reverses when the enamel begins to soften. This offers a method for determining the fusion point of enamels, but it requires considerable equipment and technique, which limits its field of application. It is reproducible within 10°F and is a definite value, which makes possible the comparison of different enamels. The results of such a test on a typical field of sheet iron ground coat compositions are shown in Figure 24.

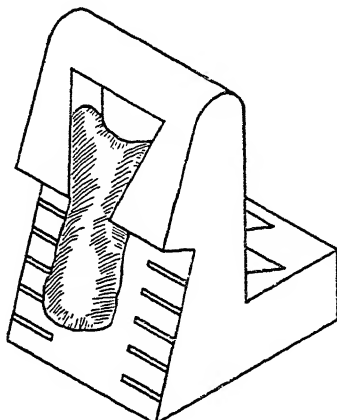


FIGURE 107.
Fusion Block.

The Temperature of Maximum Heat Absorption. When an enamel is heated through the fusion temperature zone, heat is absorbed which probably represents the heat of melting. By heating the enamel through this zone, a break in the heating curve is obtained, such as that appearing in Figure 108.

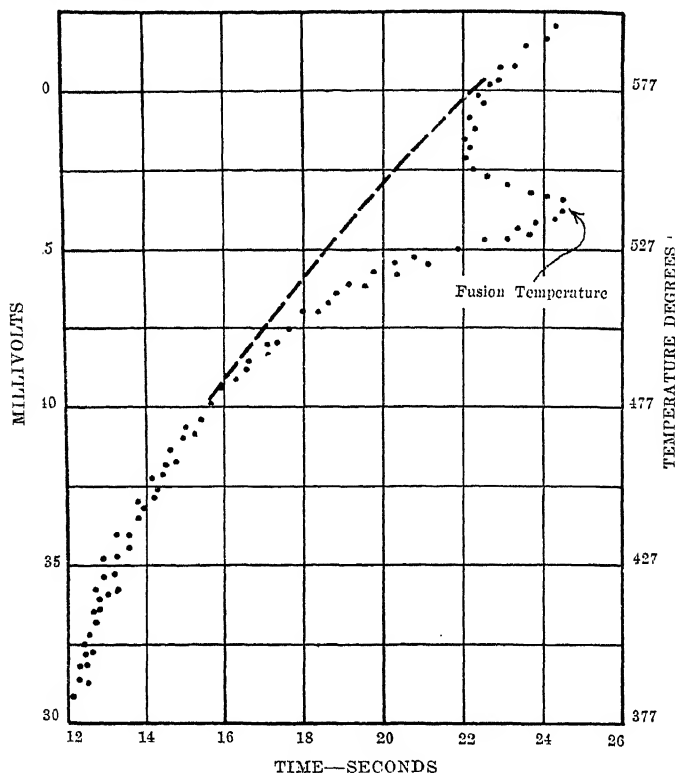


FIGURE 108.

Temperature Curve for Maximum Heat Absorption Test.

The curve shows time interval required for 2.5°C increase in temperature at the average temperature (emf) indicated by each point on the curve.

The point of maximum deflection of the curve is taken as the fusion temperature. The temperatures from the first break in the curve to the fusion temperature represent the annealing range.

To make such a test the enamel is melted in a crucible, a platinum thermocouple being placed with the junction in the center of the enamel glass. It is then allowed to cool and solidify. On reheating at a constant rate, the temperatures and times are recorded, and plotted as shown in Figure 108. This gives the data for determining the fusion temperature.

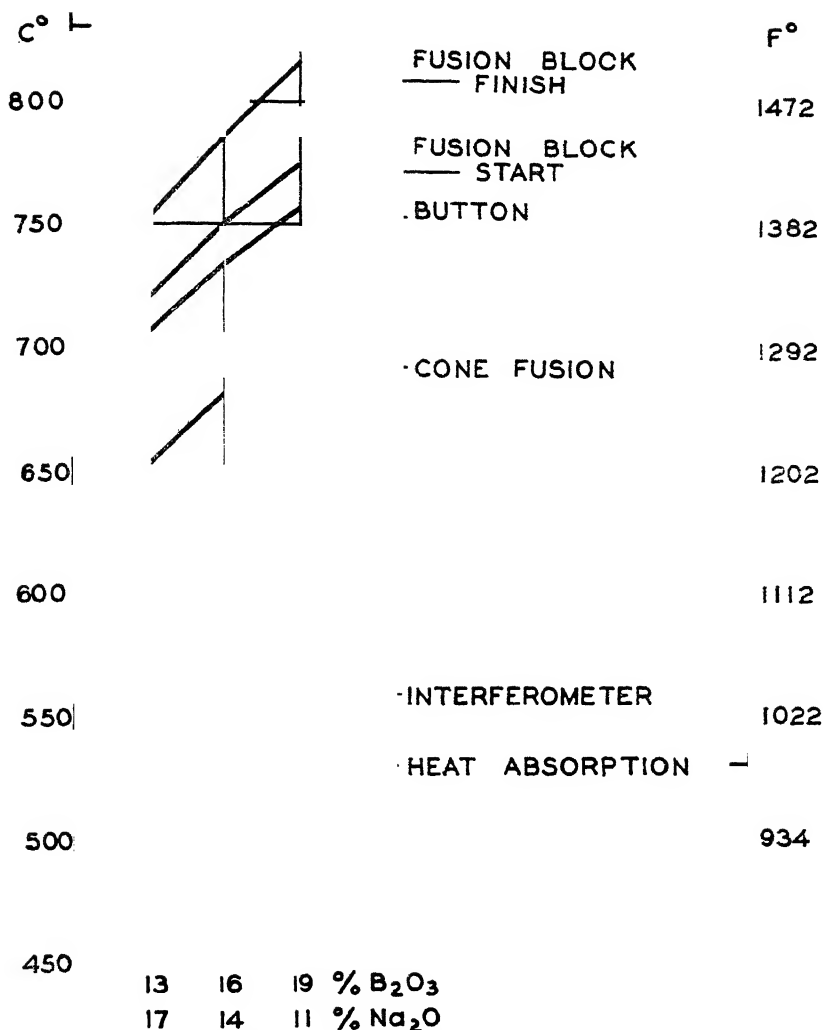


FIGURE 109. Comparison of Fusion Methods.

Frequently this test is repeated several times and values for similar points added together, thus making the interpretation more accurate because of compensating errors.

A comparison of the fusion block, the button, the cone, the interferometer, and the heat absorption tests was made by Harrison and Sweo.⁶ The relation of the different tests is shown in Figure 109. It is

⁶ W. N. Harrison and B. J. Sweo, *Bur. of Standards Jour. of Research*, 10, 189 (1933).

evident that the results of the different tests do not check, but the relation is the same from one enamel to another, with any one test. The choice of a test is dependent upon convenience, inasmuch as all give satisfactory relative results. None of the results can be considered as absolute.

The Trial Burn Test. The actual firing of enamel on test plates of metal is probably the most common control test of the enamel, not only for fusibility, but for numerous other properties. This test is also used for comparing the firing characteristics of enamels. A determination of the time and temperature producing best results, and the range of time and temperature producing satisfactory results, gives valuable information. To make such a test the trials are laid out with increasing times and temperatures, as shown in Figure 110.

FIGURE 110
PLAN FOR A FIRING TEST OF A SHEET IRON GROUND COAT

Temperature, Degrees F.	1625	OF	OF	OF	OF	OF	OF
	1600	OK	OF	OF	OF	OF	OF
	1573	UF	OK	OK	OF	OF	OF
	1550	UF	OK	OK	OK	OF	OF
	1525	UF	UF	OK	OK	OK	OK
	1500	UF	UF	UF	UF	UF	OK
		30	60	90	120	150	180

Time in Seconds

OF—overfired
UF—underfired
OK—properly fired

The thickness of the metal stock, the thickness of the enamel coating, the fineness of the milled enamel, and the characteristics of the furnace affect the results and must be controlled.

THERMAL EXPANSION AND CONTRACTION

The expansion and contraction of enamels,* with changes in temperature, are important, because the enamel must expand and contract with the metal base, subject to such conditions as elasticity, tensile strength, crushing strength, stress, and creep. Enamels do not generally have the same thermal expansion and contraction as the base metal, but are able to remain as continuous coatings, because these other factors come into play to equalize or oppose the strain. The test methods for thermal expansion are quite accurate and satisfactory.

* For complete discussion, see page 38.

The Interferometer Test. The procedure used in the author's laboratory and found to be satisfactory is as follows:

The frit is dry ground in a ball mill to pass a number sixty standard sieve and then thoroughly mixed by rolling on a square of paper. Approximately 50 grams of the mixture is then remelted in a platinum crucible in a small, vertical, platinum resistance, tubular, electric furnace.

After the glass has been held in a fluid condition, with frequent stirring, for about an hour, the temperature is lowered until the glass is sufficiently viscous to allow the drawing of a rod, approximately

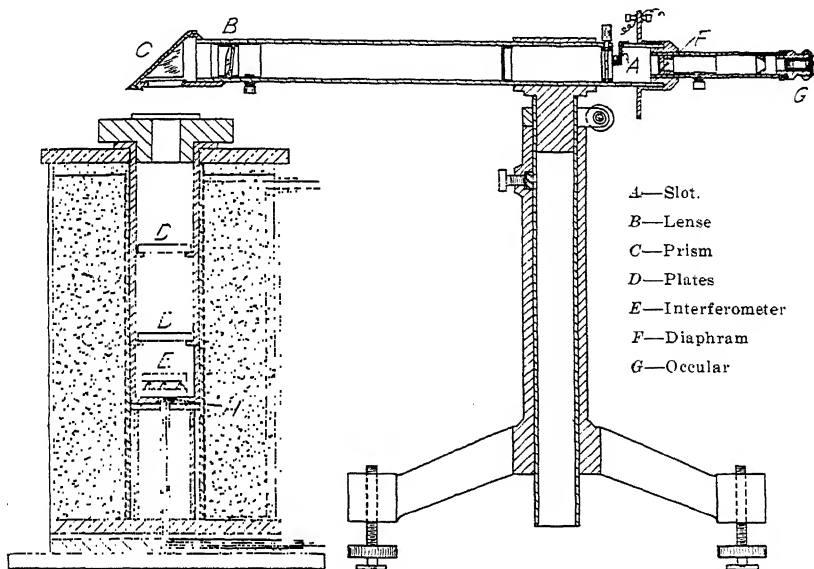


FIGURE 111. Interferometer Equipment.*

one-eighth inch in diameter, from the melt. This rod, about six inches long, is placed in an electric muffle furnace (14 by 7 by 5 inches). A small thread of the same frit, six inches long by one thirty-second of an inch in diameter, is supported in cantilever fashion at one end, and placed in the same furnace. The temperature of the furnace is then raised at a rate of twelve degrees Centigrade per minute until the thread begins to bend. The temperature is then held constant for fifteen minutes to allow for the adjustment of strains. This temperature is noted as the annealing temperature, and the sample in the furnace is allowed to cool eight hours to room temperature.

When cool, the rod is removed from the furnace and ground with

* Uni. of Ill., Eng. Exp. St., Bul. 193.

silicon carbide powder on a lap wheel, to a blunt point. The rod is then scratched with a file and broken off about one-half centimeter below the point. This process is repeated until six pointed specimens are obtained. The bases of these specimens are ground to a plane surface with a coarse abrasive and then they are further ground on a fine silicon carbide stone until the heights are the same within 0.0002 centimeter, when measured by a micrometer caliper.

The three specimens are placed between the interferometer plates, and the heights still further adjusted until there are from eight to twelve fringes in the field of view. When a satisfactory field is obtained, the specimens are removed, measured accurately by the micrometer caliper, and replaced between the interferometer plates.

The interferometer is placed in a small, vertical, chromel resistance, tubular, electric furnace. The temperature of the furnace is then raised at the rate of about eight degrees Fahrenheit per minute and the temperature at which each second fringe passes a reference point is noted. From these data it is possible to plot the expansion curve and calculate the linear coefficient of thermal expansion of the enamel.

The cubical coefficient is obtained by tripling the linear coefficient. A correction is made for the change of the index of refraction of the air in the furnace with increasing temperature. Two sets each of three specimens of each enamel are run as checks.

The equations used in calculating the data to expansions are:

$$\Delta L = \frac{N\gamma}{2} \qquad C = \frac{N\gamma}{2L\Delta t}$$

where ΔL = change in length

γ = wave-length of helium light (yellow)

N = number of fringes that passed the reference mark

C = mean coefficient of thermal expansion

t = temperature range over which measurements were taken

L = initial length.

The furnace can be calibrated in two ways: (1) by inserting a standard thermocouple among the specimens, and (2) by running a platinum specimen and calculating the temperature from the known expansion of platinum, which is accurately given in the International Critical Tables. The two methods of calibration should give the same correction values within one per cent.

A typical set of expansion curves is shown in Figure 27.

The extreme sensitiveness of the Fizeau-Pulfrich interferometer method, which permits the use of very small sizes of samples, greatly simplifies the problem of uniform heating and temperature control.

The annealing conditions and the preparation of the sample must be rigidly adhered to, otherwise consistent results cannot be obtained. Each time an enamel is reheated, it changes in composition and properties, therefore, repeat tests on the same sample cannot be run.

The Extensometer Test. The extensometer test requires an enamel rod about six inches long, which has been thoroughly annealed. This rod is placed in a vertical position in a furnace similar to the one shown in Figure 112, and the expansion is measured directly by means of an extensometer dial. The care in the preparation of the sample is the same as for the interferometer test.

The Dilatometric Method. The dilatometric method for the expansion of glass was probably developed by DuLong and Petit, who filled a glass vessel with mercury and calculated the cubical expansion of the glass by determining the amount of mercury expelled during the expansion of the glass.

During the last ten years English and Turner⁷ have employed this method for a very systematic study of the thermal expansion of simple glasses. Carefully annealed cylindrical bulbs have been used as containers for the mercury. Work has, however, been limited to temperatures below one hundred degrees Centigrade.

The Enameling Test. A test of the thermal expansion and contraction of

enamels which has offered some promise is that of measuring the distortion of the metal by the enamel. In cooling a sheet of light gauge metal, which has been fired with an enamel on one side only and which has a different thermal contraction from the iron, a warping to or away from the enamel is noted. This can be used as a basis for determining the thermal expansion and contraction of the enamel. Such a test was conducted in the author's laboratory, in which strips of 30

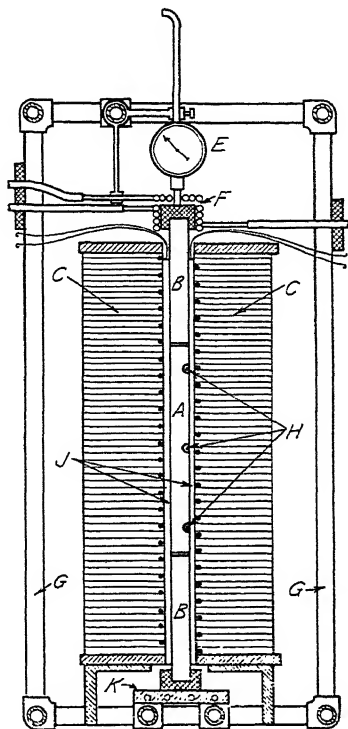


FIGURE 112. Extensometer.
A, Specimen; B, Quartz rods; C, Insulation; E, Dial; F, Insulating Coil; G, Frame; K, Support.

⁷ Jour. Soc. Glass Tech., 3, 239 (1919).

gauge metal were enameled on one side only and then heated in a vertical position, the deflection being measured with a cathetometer. Although not yet developed to an exact method, it shows promise. W. N. Harrison reported a similar test in which metal rings about one inch wide and three inches in diameter were enameled.⁸ They were then cut open and reheated, the opening and closing of the rings being

a measure of the unequal expansion and contraction of the enamel and the iron. These results are very promising, since the actual conditions that exist when enameled ware is heated and cooled are simulated, and the relation is followed throughout the whole range of temperature. This test, applied to ceramic bodies and glazes, was first tried by Schurecht and Pole.⁹

THERMAL SHOCK

Enamels have an advantage over most finishes in that they will withstand relatively high temperatures and repeated heating and cooling without deterioration. The rate of temperature change or the thermal shock which enamels will withstand is limited, however, and varies with different enamels. Few enamels will withstand severe thermal shock, but a good enamel surface should be resistant. The earliest tests on resistance to thermal shock were applied to kitchen ware. Small enameled dishes were heated and quenched in water. The temperature of heating controlled the severity of the test.¹⁰

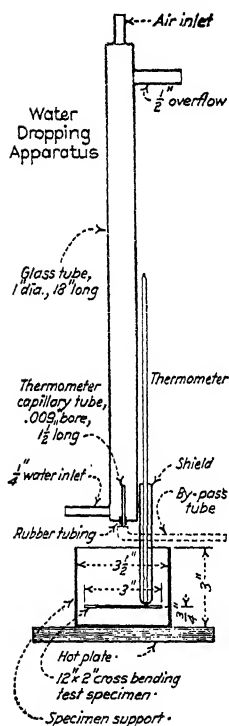


FIGURE 113.
Water Drop Test
Apparatus.

The Water Drop Test. One of the most recent tests on the thermal shock of enamels is the water drop test,¹¹ which consists of heating the specimens of enameled iron to 360° C (680° F), and causing water to drop on the enameled surface at a constant rate of one drop every twenty seconds for a period of thirty minutes. The apparatus used is shown in Figure 113. The test is made by placing the test piece over the hot plate and allowing the water to start dripping on it as soon as

⁸ Meeting of the American Ceramic Society, February (1934).

⁹ H. G. Schurecht and G. R. Pole, *J. Am. Ceram. Soc.*, **13**, 369 (1930).

¹⁰ R. D. Landrum, *Trans. Am. Ceram. Soc.*, **14**, 489 (1912).

¹¹ C. J. Kinzie, *J. Am. Ceram. Soc.*, **12**, 188 (1929) and also E. H. Shands, *The American Enameler*, April-May (1932).

it reaches the temperature of 360° C. The results can be classified as (a) no attack, (b) slight crazing, (c) severe crazing, and (d) chipping.

The Quench Test. Other tests for thermal shock include those in which test plates are heated to various temperatures and quenched by immersing them in baths of water, oil, and molten salts. Sodium nitrate, the eutectic mixture of sodium nitrate and potassium nitrate, or the ternary eutectic with calcium nitrate are quite suitable for the molten salts. The test is not severe, and has the objection that the quenching test is run above the temperatures at which the enamels are ordinarily used. The use of an oil or an air-oil emulsion is quite satisfactory, but is troublesome, since the emulsion tends to break when heated.

In some tests, the enamel test piece is subjected to steam, running water, or an airblast. None of these latter tests have been standardized, but they show that the possibilities for developing a satisfactory heat shock test for enamels are very good.

THERMAL CONDUCTIVITY

The thermal conductivity of enamels is important from both the scientific and the practical viewpoint. A fundamental study of firing necessarily involves the radiating, reflecting, and conducting powers of the enamels. Little has been done on the subject from this standpoint, but considerable effort has been expended on the more practical side of the question. The conduction of heat through enameled surfaces in service is important to the kitchen ware industry. As a reflector of heat, enamel is important in the stove, refrigerator, and building industry.

As described on page 46, the thermal conductivity of a glass is approximately an additive function of the composition, the factors being given in Table 2.

In a series of tests on enameled steel tanks, Poste¹² published the values in Table 48, which represent actual service conditions.

The values for the thermal conductivities of glasses, as given by the International Critical Tables,¹³ vary from 1.812 to 3.243 g-cal cm² seconds at 100° C, and from 1.698 to 2.796 g-cal per cm.² per second at 0° C.

Comparisons¹⁴ between the thermal conductivities of enameled iron and insulite have been made to determine the suitability of enameled

¹²E. P. Poste, *J. Ind. and Eng. Chem.* 16, 469 (1924).

¹³International Critical Tables II, 101.

¹⁴Preliminary Investigation of Thermal Properties of Porcelain Enameled Steel, Enamel-ist, 11 (5) 11 (1934).

iron for building construction. These tests consisted of determining the relative amounts of heat escaping from, and also entering, two boxes, 3 x 3 x 1 foot, one constructed of one-half inch insulite and the other enameled eighteen gauge iron.

The results showed that one-half inch of insulite is far better where radiant heat is concerned, the thickness of the enamel coat not being an important consideration. The enameled box is reported as being two-thirds as efficient as one-half inch of insulite in preventing heat

TABLE 48
OVER-ALL COEFFICIENTS OF HEAT TRANSFER

<i>Conditions</i>	<i>Kg. Cal per Hr.¹² Sq. M. Per °C.</i>	<i>Btu per Hr. Per¹² Sq. Ft. Per °F.</i>	<i>Over-all¹² Coeff. Heat Transfer per °C.</i>
Steam, to water heated.....	400-700	80-140	1674-2929
Hot water, to water being heated.....	350	70	1464
Steam, to boiling water.....	700	140	2929
Steam, to a thick fruit product...	160	32	669
Cooling hot water, by cold water and brine.....	200-600	40-120	837-2510
Hot oil, to oil being heated.....	65-140	13-24	271-586
Hot oil, to boiling water.....	150-200	30-40	628-837
Steam, to water being heated in tubular heater.....	500-800	100-160	2092-3347
Steam being condensed to water in a tubular condenser jacket	700	140	2929

escaping from the interior of a house to the outside, and roughly one-half as efficient in keeping sun heat out.

Other methods which can be used for determining the thermal conductivity of enameled iron are boiling tests in enameled pans of different types. Temperature gradient tests made by placing thermal elements in the iron, in contact with the iron, in the enamel, and at the surface of the enamel, call for fine technique, but would undoubtedly lead to valuable data. With the ever-broadening uses of enamels more data are needed on the thermal conductivity.

MISCELLANEOUS

Other thermal properties, such as specific heat, radiation and reflection coefficients, have not received extensive investigation and little is published concerning them. Winkelmann and Schott established the specific heats based on the values of the individual oxides as described

¹² International Critical Tables II, 116.

on page 45. The data on enamel glasses is, however, very limited. White¹⁶ gives values of from 0.20 to 0.30 gm. cal. per °C, and Maurach¹⁷ values of 0.32 gm. cal. per °C for glasses. The values given for glasses in the International Critical Tables¹⁸ range from .1881 to .2640 gm. cal. per °C, invariably increasing with an increase of temperature. The values for enamels are probably similar to these. They do not have commercial importance at present, since the heat balances of enamel smelters and furnaces involve so many other unknowns that these values would add little, if accurately known.

The radiation, or thermal emissivity,¹⁹ of white enameled surfaces is nearly the same as that for white lead paint.

OPTICAL PROPERTIES

The most important optical properties of enamels are the color, the so-called opacity, and the gloss. In Chapter 3 the subjects of opacity and color are discussed in detail; therefore only the tests will be described here.

OPACITY AND COLOR

In the consideration of vitreous enamels the terms opacity and color have to do with the appearances. Opaque enamels are in reality translucent and not opaque. The term opacity, as applied to enamels, has come to mean the appearance of a pleasing white surface. If the surface is mottled by a poor distribution of the opacifier, it is not opaque from the enameleer's standpoint, as the appearance is not pleasing to the eye and it is considered glassy.

Methods. Many methods have been developed for determining the opacity and color of enamel coatings, but the principle of all the tests is the same. The enamel surfaces are compared to a perfectly white surface (magnesium oxide is taken as standard). The comparisons are made at different wave lengths throughout the visible spectrum, and the percentage reflection of each wave length is plotted in Figure 114.

If the enamel is not pure white, the data show which color predominates. A pure white enamel should produce a fairly straight line on the chart at seventy to eighty per cent reflection. A blue white is high at the blue end and a yellow white is high in the yellow area. Colored enamels can be analyzed to show the predominating and contributing colors. The curve for a blue enamel is shown. This blue is very pure and contains very little yellow, green, or red.

¹⁶ W. P. White, *J. Am. Chem. Soc.*, **116**, 133 (1919).

¹⁷ H. Maurach, *Berlin U Munchen*, (1923) S 83.

¹⁸ International Critical Table, II, 101; *Am. J. of Sci.*, **47**, 1 (1919).

¹⁹ Coblenz and Hughes, *Bur. of Std., Tech. Paper*.

The Spectrophotometer. The spectrophotometer gives complete information concerning the color and opacity. Sample plates of the enamel in question are made and compared to magnesium carbonate. The spectrophotometer is shown in Figure 114. The sample and the standard are placed side by side in the lamp chamber and the light from the condensed filament lamp is reflected through the opening to the instrument in two beams, one from the sample and the other from the standard. Both beams of light enter the telescope and pass through the prism, which refracts only a small range of wave lengths of light through the other arm of the telescope to the eye. By rotating the prism, the wave length of the light reaching the eye can be varied over

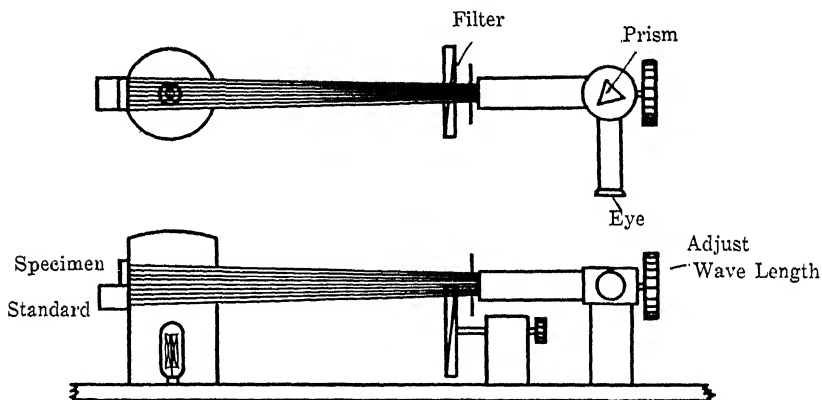


FIGURE 114. The Spectrophotometer.

the whole visible spectrum. Since the position of the prism is graduated on a scale, the wave length can be read off the dial at any time. A rotating perforated disk acts as a filter to allow either all or any part of the light from the standard to pass into the telescope. This is graduated to indicate the percentage which is allowed to pass through the telescope to the eye.

To operate the instrument, tests are run at different wave lengths by adjusting the prism to the different positions. On looking through the eyepiece the field of view appears as a split field, the upper half representing the standard and the lower half the test specimen. The rotary filter is adjusted until both halves of the field of view have the same intensity and the scale on the filter adjustment is read. This is repeated for the different wave lengths of the spectrum and the data so obtained are plotted as shown in Figure 115.

Recording Color Analyzer. A recording color analyzer eliminates the personal factor in comparing the intensities of the beams of light from the standard and the sample. It uses a photo-electric cell, which controls the adjustment of the instrument and makes an automatic record of the reading.

The Reflectometer. Since the instruments already described are expensive and quite complicated, a simpler instrument is often used for checking the opacity or reflecting power of white enamels. The

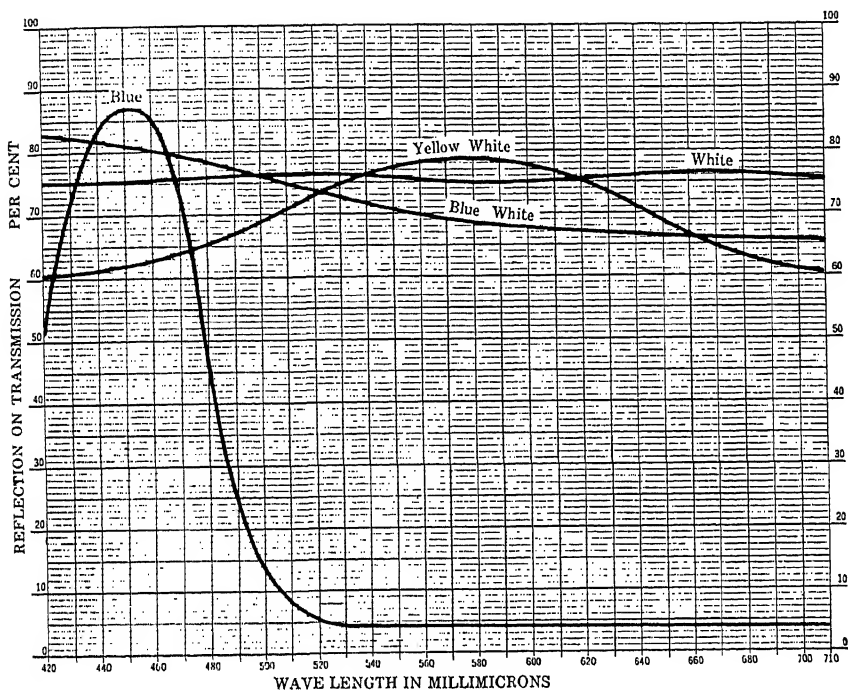


FIGURE 115. Enamel Color and Opacity Values.

instrument devised by A. H. Taylor²⁰ is one of the most suitable instruments of this type. Taylor describes this instrument as follows:

It consists of a 4-inch hollow sphere (the reflectometer) attached to a Macbeth illuminometer (a portable photometer). A tube containing lenses and a small flashlight lamp rotates about an axis in one side of the sphere. It projects a beam of light onto the test surface or the sphere wall. The photometer measures the brightness of the sphere wall at a spot screened from the test surface. The ratio of the photometer readings with the light directed first onto the test surface,

²⁰ General Electric Company, Enamelist, 8, (12) 16 (1931); Bur. of Std. Scientific Paper, Nos. 391 and 405; J. of the Opt. Soc. of Am., IV (1) (1920).

then onto the sphere wall, gives directly the diffuse reflection-factor of the test surface. The measurements are not affected by the way in which the light is reflected by the surface; i.e., whether the surface is a mirror or a diffusing surface. When the apparatus is set up only a few minutes are required for the measurement, and extensive tests have shown the results to be quite accurate. The apparatus is portable.

A less accurate method, but one requiring less apparatus may be used if objects of only one type, e.g., enameled metal, are to be tested. The author has found that when a diffusing surface such as magnesium carbonate, white plaster, porcelain enameled metal, etc., is illuminated by light incident perpendicular to the surface, the brightness of the object in a direction fifty degrees from the perpendicular is very closely proportional to the diffuse reflection-factor of the object. Hence if a photometer is arranged to measure the brightness of objects in this direction, when illuminated normally, various flat objects can be directly compared. Magnesium carbonate has been found to have a diffuse reflection-factor of approximately 97 to 99 per cent, hence a block of this material can be used as a standard for evaluating the reflection-factors of enameled objects. Tests made with six specimens of porcelain enamel showed that this method gave results correct to approximately 5 per cent of the reflection-factor. This method cannot be applied to the measurement of reflection which is largely specular, such as that from oxidized aluminum.

If the highest possible accuracy is desired, and all types of surfaces are to be measured, the sphere reflectometer is the only one which will give the desired results.

A crude method of measuring the opacity is one in which the enamel is compared to a series of standards. This is better than no test, but the unaided eye often becomes confused in such tests. However, finished ware is sometimes tested by visual comparison under a good light.

INDEX OF REFRACTION

The index of refraction of glasses and enamels affects their brilliance. The index of refraction may be defined as the ratio of the sine of the angle of incidence to the sine of the angle of refraction. The index of refraction has in many cases been used to explain the opacity of enamels, but the variation in most compositions does not seem to be great enough to have an important influence. Since all opacifiers have high indices of refraction, it might be concluded that an enamel glass with a low index would be the most desirable for developing opacity. The author has tried to prove this assumption, but without success. High-lead and high-barium glasses have higher refractive indices than those low in these constituents. The index of refraction in glasses shows a tendency to increase with the specific gravity.

The index of refraction of enamels can be measured by means of a microscope. Knowing the thickness of the enamel coating and then

measuring the change of focus from the top to the lower side of the enamel the index of the glass can be calculated. This method can, however, be used only on transparent glasses.

Another and more common method for determining the index of refraction of enamels is the "Becke Method". In this method the enamel or glass is crushed to fine particles and placed on a slide with an oil of known index of refraction. The index of the glass is then compared to that of the oil by first bringing it into focus and then slowly elevating the barrel of the microscope. A line of light appears at the edges surrounding the grains of glass, and then, as the microscope is raised, it moves into the medium having the higher index of refraction. By comparing the glass particles to a series of known oils, its index is located between two of them, and thereby determined.

Parmelee and Ehman²¹ describe the use of a refractometer in the determination of the index of refraction of glass by total reflection as follows:

This method is based on the principle that light cannot always pass from an optically dense into an optically rarer medium, since at a certain angle, known as the critical angle, it will suffer total reflection. The critical angle for any substance varies with the index of refraction of that substance. This method is particularly useful because the measurement can be made upon a single polished surface, which may be quite small in area.

The measurement is made by means of an instrument known as a total refractometer. The essential feature of this instrument is a hemisphere of glass with a known high index of refraction. The upper surface of the hemisphere is plane, and accurately adjusted in a horizontal position. The glass or mineral to be tested may be of any shape provided that some one surface upon it is ground plane and polished. A drop of some oil with an index of refraction intermediate between that of the glass hemisphere and the glass whose index is to be determined, is placed between the surface of the hemisphere and the flat surface of the glass.

By means of a mirror, a beam of sodium light is thrown upon the hemisphere. At the critical angle for the combination of the two glasses (the effect of the oil film can be ignored) a shadow will appear in the field of vision. One side will be illuminated by the total reflection of all rays beyond those of the critical angle, while the other side will be distinctly darker, since here a considerable amount of the light passes out into the glass. As the index of refraction of the glass hemisphere is known, the index of the second glass can be calculated from the measured critical angle by use of the formula:

$$n = \sin un^i$$

where n is the unknown index, u , the critical angle measured, and n^i , the index of the atmosphere.

²¹ J. Am. Ceram. Soc., 13, 475-88 (1930).

MICROSCOPIC EXAMINATION

The microscope has many possibilities both in research and in the control of enamels, but its use has been very limited. In the study of raw materials, the processing, and the finished product, the microscope is a useful tool. The use of the metallographic microscope has greatly aided in the development of better enameling irons. The control of the raw materials used in the making of enamels can be improved by the use of the microscope. The petrographer, mineralogist, and the chemist have contributed extensively to the methods of using the microscope for these purposes.

The examination of enamels, both during processing and in the finished state, offers a very promising field for the use of the microscope. Much has been done in this direction and it is believed that considerable progress will be made in the future.

Metallography. The methods of metallographic study will not be described here, since they are available elsewhere to anyone seeking the information. It is important, however, that the technical enameler be well founded in the principles of metallography.

Raw Materials.²² The microscopic examination and identification of raw materials have long been used to a limited extent in control and research. A petrographic microscope and a few reagents make it possible to do considerable work of this nature. Inasmuch as the raw materials used in enamels are quite limited in number, a specialized technique for these can be developed without going extensively into the field of petrography.

Feldspar, for example, is the only enamel raw material which, when examined between crossed nicols and transmitted light, shows a network of fine parallel lines or in some cases light and dark bands.

A method devised by Booze and Klein²³ is used to determine the relative amounts of feldspar and quartz in a sample of commercial feldspar. It is based on the differences in the fusion points of the two minerals. The commercial spar is heated to a temperature high enough to melt the feldspar and not dissolve the quartz in the molten mass. The sample is powdered and then examined under the microscope with crossed nicols, whereupon the isotropic feldspar appears dark and the quartz grains, due to the interference colors, are visible. On comparing with samples containing known percentages of quartz the amount in the unknown feldspar is determined.

²² E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, John Wiley and Sons, (1931); J. T. Irwin, *The Enamelist*, 6, (8) 18-28 (1929).

²³ M. C. Booze and A. A. Klein, *J. Am. Ceram. Soc.*, 6, 698-703 (1923).

A modification of this test which gives improved results is that described by Parmelee and McVay.²⁴ In place of using the powdered feldspar, thin sections were made and the relative amounts of quartz and feldspar were measured, using a Wentworth screw micrometer.

A further investigation of the different feldspar minerals present in commercial spars is fully described by Insley.²⁵ Since feldspar is one of the enameleer's more important raw materials, and since its composition both chemically and mineralogically is likely to vary, a petrographic analysis is very helpful.

Fluorspar can be readily identified under the microscope, for it is the only isotropic crystalline mineral used as an enamel raw material. The characteristic of isotropic minerals under the microscope is that they do not appear at all when placed between crossed nicols. In the examination of commercial fluorspars the impurities such as quartz and calcite show under crossed nicols. This offers a method of detecting the presence and amount of these impurities. By using measured amounts of the standard fluorspar and the unknown fluorspar and placing them between cover glasses with the same amounts of Canada balsam, a direct comparison can be made.

Eryolite powder, when examined between crossed nicols, appears as light gray, uniformly colored crystals. It is only weakly refractive and, therefore, does not transmit any large amount of light. It, however, has the same index of refraction as absolute alcohol, so that, when immersed in alcohol and examined in transmitted axial light, it is barely visible.

Rather than depend entirely on the microscopic analysis, the identity of eryolite or fluorspar can be further confirmed by placing the material in a small platinum or lead crucible with sulphuric acid and covering with a cover glass. Both fluorspar and eryolite will evolve hydrofluoric acid which will attack the glass. This is a definite identification of a fluoride.

Barium and calcium carbonate both evolve carbon dioxide when heated with hydrochloric acid, in which they dissolve completely. When neutralized and treated with sulphuric acid, they will give white precipitates of the sulphates.

These sulphates are, however, quite different when observed under the microscope. Barium sulphate appears under the microscope as a finely crystalline meal, while the calcium sulphate appears as starlike clusters of crystalline needles.

²⁴ C. W. Parmelee and T. N. McVay, University of Illinois, Eng. Exp. Sta. Bul. 233 (1931).

²⁵ H. Insley, J. Am. Ceram. Soc. 10, 651 (1927).

Zinc oxide should dissolve almost completely in dilute hydrochloric acid. If a drop of potassium mercuric thiocyanate solution * is added to this acid solution, the zinc separates out as cross-shaped crystals with feathery edges.

White lead and litharge are readily dissolved in dilute nitric acid. A drop of potassium iodide solution, added to this acid solution of the lead on a microscopic slide and warmed, forms small six-sided yellow plate-like crystals of lead iodide. These crystals, which should be examined immediately, are quite characteristic.

Many other microscopic tests on the raw materials used in making enamels can be developed by a careful study of this subject.

Surface Phenomena. The use of the microscope to study the surface of enamels has long been practiced. An enamel under magnification is shown to contain many entrapped bubbles and, if the enamel is

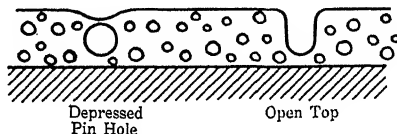


FIGURE 116. Pin holes.

transparent, these bubbles are quite obvious. Transparent sheet iron ground coats can be examined advantageously with a long focus microscope, of the binocular type. The surface, the bubble layer, and the inter-face with the iron can be readily seen, if the enamel does not contain considerable quantities of iron and nickel oxides. The iron surface in many cases is very distinct, showing the crystals as though it had been etched. The bubbles in a good sheet iron ground coat should not approach the thickness of the enamel layer in size and they should be uniformly distributed. An enamel which is underfired shows many large bubbles, often extending to the surface and causing defects, such as pin holes and blisters. If the bubble has just burst through the surface, it causes a blister, but, if the firing is stopped just as the bubble reaches the surface, a pin hole is formed. The pin hole appears as shown in Figure 116. The gases in the bubble contract as the enamel is cooled, sucking an indentation into the surface of the enamel. In some cases, the enamel at this point fails and the pin hole extends to the bottom of the bubble, as shown in Figure 116.

The examination of enamels attacked by acid, alkali, weather, or soil may show either of two effects. If the enamel is somewhat soluble,

* Make the potassium mercuric thiocyanate solution by mixing concentrated solutions of equivalent molar weights of potassium thiocyanate and mercuric chloride.

the surface is etched and it looks like powdered glass. The outer surface can be readily scratched away, exposing the enamel beneath, which has a rough etched surface.

If the enamel is resistant to solution, the attack may give the appearance of crazing (many fine cracks). The surface does not show etching when observed under the microscope, but rather one characteristic of heat check. The whole surface is interwoven with many fine craze lines. The author believes that the soluble part, being the last to solidify in this type of glass, is confined between the larger particles of glass. The solution, therefore, takes place only in the boundaries around the more resistant glass. This theory is partially verified by the fact that an enamel so attacked can be fused down if refired, after which it is no longer subject to the attack of the solvent. In some cases this treatment of an enamel with acid and then refiring has produced acid-resistant enamels.

The white cover enamels are more difficult to observe under the microscope than the ground coats. Defects such as specks, blisters, uneven opacity, seum, and attack by solution can be very readily studied. The studying of defects in enamels by means of a microscope offers a field for considerable ingenuity, each case having its own peculiarities.

Cross Sections. The examination of cross sections of the enamel coating and the metal base has received considerable attention. This method of microscopic examination makes possible the study of the adherence mechanism, bubble distribution, iron oxide penetration, copper-heads, fishscale, firing phenomena, and reboiling. It will probably add greatly to our future knowledge of enamels.

The technique of preparing the sample for examination is of as great importance as the examination itself.

The Preparation of the Sample. The sample is carefully selected to show advantageously the defect or area to be examined. It is then cut with a hand hacksaw, the enamel plate being placed between two pieces of soft wood to minimize chipping during the operation. It is next mounted for grinding and polishing either between layers of celluloid, or in sealing wax, or some low melting alloy. Samples mounted in this manner are shown in Figure 117. These procedures in mounting are necessary to minimize the chipping of the enamel when grinding and polishing.

The sample is filed down flush with the protecting layer by moving the file over the surface, at a 45-degree angle, from the enamel side to the metal side. The specimen is next ground on an emery cloth disk in

a direction at 45 to 90 degrees from that used with the file, but always from the enamel side to the iron base metal. The speed of this grinding should be about 800 rpm.

A paraffin disk is used to polish the sample. This polishing is first carried out with levigated alumina, suspended in a soap solution. The grinding is again at 45 to 90 degrees from that of the previous operation, but also in the direction from the enamel to the iron. Best results are obtained with a high speed wheel (1800 rpm), because this gives a more even level between the enamel and the iron. All scratches from previous operations are removed.

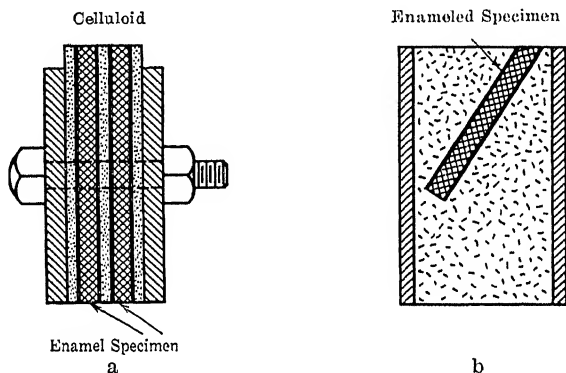


FIGURE 117. Method for Preparing Cross Sections.

The final polishing is carried on with jeweler's rouge on a disk covered with billiard-table cloth. Polishing is continued until all scratches are removed from both the enamel and the base metal.

Examination of the Sample. The examination is best made with the inverted metallurgical type microscope, at magnifications of from 600 times up to 1000. The illumination is important, decentered critical illumination being most satisfactory.²⁶

MISCELLANEOUS

The Gloss. The gloss and the effects of ultraviolet light, polarized light, and X-rays have received some attention by the enamer. The gloss has been determined by the use of a glarimeter, but the work has not been extensive. Polarized light is used to determine the strains in glass, but it has not been used for vitreous enamels. Since enamels are applied to iron, the importance of conducting ultraviolet light is remote, although the reflection factor might be of importance.

²⁶ J. O. Lord and W. C. Rueckel, *J. Am. Ceram. Soc.*, **14**, 777 (1931); G. W. McGohan, *J. Am. Ceram. Soc.*, **15**, 389 (1932).

X-Ray Methods. X-rays have been used to advantage in studying the fundamentals of enamel opacity by determining the crystalline compounds present. An X-ray analysis of an enamel consists of passing the X-rays through either a small thread of enamel glass or powdered enamel in a capillary tube, or by reflecting the X-rays at the surface of the enameled sample. The rays leaving the sample are photographed and the pattern obtained is compared with known materials. Since no two materials produce the same patterns, this represents a positive identification of the compounds present. X-rays have the characteristic of darkening white enamels, the colors ranging from a sepia to a brown or gray. This has been used in the laboratory to make designs on enamel, lead being used as a stencil, shielding part of the enamel surface from the X-rays.

The possibilities of further studies on enamels, in which X-rays will play an important part, are great and will probably lead to valuable information. An X-ray study of the processes of smelting and firing, a further study of adherence and the raw materials should be made.

PHYSICAL AND MECHANICAL PROPERTIES

The physical and mechanical properties of enamels, such as the adherence, the rate of cooling, the development and relief of strains, the strength of the finished ware, and the resistance to impact, are influenced by the metal base on which they are fired. Because of this influence, the metal must be considered in many physical tests both from the standpoint of preparing the sample and of the actual test itself.

ADHERENCE

A discussion of the mechanism of adherence of enamels to iron is given on page 166, therefore, the following will be limited to the testing. Two types of tests are used for measuring the adherence: (a) metal deformation tests, and (b) tests in which the metal does not deform.

Metal Deformation Tests. In the metal deformation tests the metal base is actually deformed through its yield point, so as to give permanent deformation.

Bending Test. The simplest and oldest test of this type is that of bending samples through an angle of 90 to 180° and noting the effect on the enamel layer on the outside of the bend. The amount of enamel chipping off, and the nature of that adhering are important. If the enamel scales off clean, the adherence is shown to be very poor; if the surface of the metal is well coated with slivers of firmly adhering

enamel, it is good. All degrees between these extremes are experienced. Such a test should be standardized and comparison samples used. The thickness of the metal, the metal properties, and the thickness and the firing of the enamel must be standardized.

Refinements of this bending test have led to the impact tests, i.e., (a) the falling weight test, (b) the swinging hammer test.

Falling Weight Test. The falling weight test is the most popular test for adherence at the present time. It gives definite results and can be modified to meet existing conditions. Such a test developed by C. J. Kinzie²⁷ is as follows:

The apparatus, which is shown in Figure 118, consists of a brass tube which can be easily adjusted as to distance between the lower end of tube and the specimen. Through the walls of the tube, at spacings of three inches, are drilled holes so that the stop-pin can be set at any desired height above the specimen. A 1-inch diameter steel ball weighing about 67 g. is used. If a heavier weight is needed, a larger diameter tube can be used. We have used, in addition to the tube shown, a larger tube taking a 1½-inch diameter steel ball weighing 225 g.

The procedure in making tests is as follows:

The specimen is placed and the tube is adjusted so that the ball will just clear the space between surface of specimen and lower end of tube. The pin and ball are placed in position, 25½ inches above the specimen, and by withdrawing the pin the ball is permitted to drop onto the specimen. This operation is repeated 10 times at 10-second intervals and the result observed.

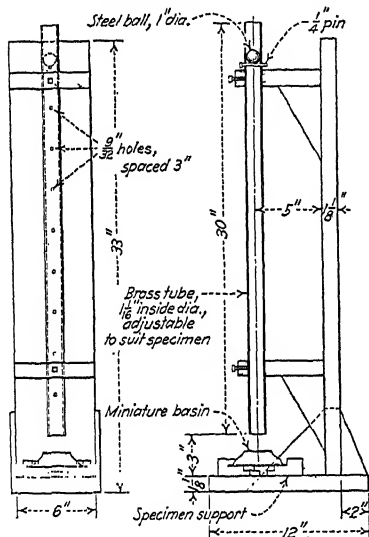


FIGURE 118.

Falling Weight Apparatus.

that the test piece may either rest on a solid metal surface, or a block with a hole in it directly under the point where the weight strikes the specimen. In some cases a heavier weight, supported between two guide rods, is used and one impact only is required to make a test. The degree of enamel adherence must in any case be judged by comparison with standard samples.

Pendulum Test. An impact machine of the swinging-hammer type is described by R. H. Turk.²⁸ The general construction of the machine is shown in Figure 119.

²⁷ C. J. Kinzie, *J. Am. Ceram. Soc.*, **12**, 188 (1929).

²⁸ R. H. Turk, *J. Am. Ceram. Soc.*, **13**, 887 (1930).

It has a pendulum arm two feet in length, carrying a weighted hammer or bob. The arm is kept rigid by a system of guy wires, and is fastened to a short shaft turning in ball bearings. The ends of the shaft are turned to a point and hardened. The caps at the ends of the bearing boxes are hardened and are just brought

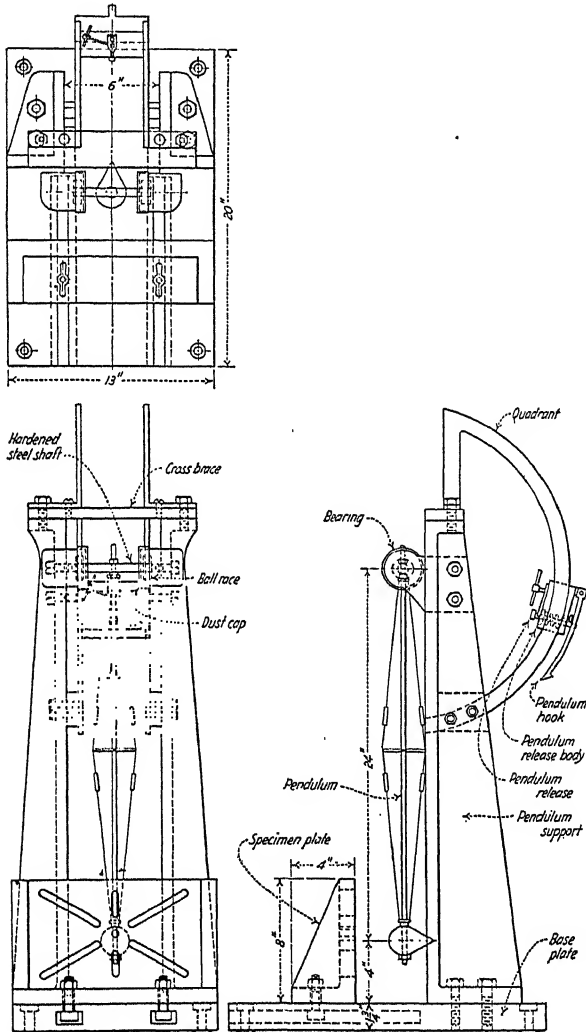


FIGURE 119. Pendulum Test.

in contact with the pointed ends of the shaft to take up end play. Friction is negligible, as the bearing surface is very small. By lifting and suspending the pendulum as described, each blow is delivered at the same place upon the test piece.

The release mechanism slides on two quadrants, graduated so as to give blows in increments of 0.05 foot-pound with the one-pound hammer. A catch engages notches in the quadrants, holding the release device. A forked hook engages the cross-bar on the pendulum arm and holds the pendulum until released by tripping a spring which causes the hook to snap back.

Two hammers are used, weighing one and two pounds, respectively. They are pear-shaped and have a hardened striking face of one-inch radius. By changing hammers, blows equivalent to four foot-pounds, as a maximum, can be delivered. The two-pound hammer is used mostly for cast iron enamels and the one-pound hammer is used for sheet iron enamels.

The standards are heavy, rigid castings, as is the base of the machine. A heavy cast iron angle plate slides in a milled slot in the base and is adjustable along the length of the machine to take care of samples of varying depth. A hole is drilled into the angle plate in line with the hammer when it hangs free to facilitate observation of failure of sheet iron samples.

All castings are extra heavy to assure a rigid, vibration-free machine; leveling screws are in the base. Clamps are built into the angle plate and are so designed as to take care of almost any shaped sample.

Graduation of Machine. The weight of the pendulum of the machine when constructed as specified is four ounces. As the arm is symmetrical in form its weight can be considered as concentrated at the middle point. Therefore, the following formula is applied:

$$H = \frac{I}{W + \frac{w}{2}}$$

where H = height of hammer

I = impact in ft.-lbs.

W = weight of hammer (lbs.)

w = weight of arm (lbs.)

From the point of contact of the height, H, and an arc described by the hammer, a line is projected to the center of the bearing shaft. The quadrants are graduated where this line crosses them.

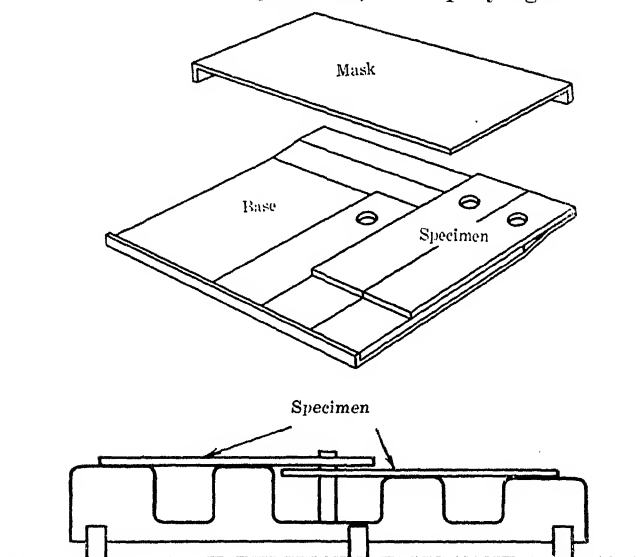
Method of Making the Test. The test specimens are made either in the shape of rectangular sheet iron trays $7\frac{1}{8} \times 4\frac{3}{4}$ inches in size or cast iron panels $6 \times 3\frac{1}{2}$ inches in area and $\frac{1}{8}$ inch thick. These enameled samples are clamped in place, the actual position of the impact depending on the conditions desired.

To make the test, the pendulum is allowed to drop from various positions. Failure is indicated when the enamel breaks away over a specified area such as $\frac{1}{4}$ of an inch in diameter. The breaking position of the pendulum on the quadrant is usually taken as the indication of the impact resistance. A number of individual results are averaged to give accurate results.

Tests in Which the Metal Does Not Deform. The tests in which the metal does not deform are more complicated than those in which it does. The results are, however, more nearly characteristic of the actual adherence and should, therefore, be further developed.

Plate Test. The method of lapping two pieces of enameled metal together in the furnace so that the enamel acts as a bond between the two pieces and then determining the force necessary to pull the cooled pieces apart has been fully described.²⁹

The enamel is applied to the specimens by placing them in an apparatus, as shown in Figure 120, and spraying the enamel. The



FIRING SUPPORT

FIGURE 120. Plate Test Apparatus.

enamel is then dried and the samples are placed in the support, shown in Figure 120, for firing.

The specimens are so placed that the enamel surfaces face each other, but do not touch. They are fired in this position until the boiling has ceased. They are then clamped together in the center by suitable tongs and removed to an annealing furnace at 500° C and allowed to cool slowly.

The samples are then placed in a tensile strength machine, the grip being made through the holes in the metal stock. The failure of the contact is a result of both tension and shear, which are too compli-

²⁹ W. N. Harrison and G. T. Thaler, *J. Am. Ceram. Soc.* 11, 803 (1928).

cated to be analyzed. The results show failure at the contact of the enamel and the iron, or failure within the enamel layer. The former is the desired result, in which the metal is left bright and clean; the latter shows either adherence greater than the strength of the enamel, or enamel which is mechanically weak. This weakness may be caused by improper annealing or manipulation.

TABLE 49
ADHERENCE VALUES²⁹

Values Obtained in Seven Consecutive Tests with a Standard Cobalt Ground Coat, and with the Same Enamel Without the Cobalt, Manganese and Nickel Oxides

Test No.	ENAMEL CONTAINING COBALT, MANGANESE AND NICKEL OXIDES		SAME ENAMEL WITHOUT COBALT, MANGANESE AND NICKEL OXIDES	
	Load at Failure (lbs.)	Failure in Bond (Per cent of Clean Metal Exposed)	Load at Failure (lbs.)	Failure in Bond (Per cent of Clean Metal Exposed)
1	910	60	470	100
2	830	75	490	100
3	880	25	410	100
4	1000	80	320	100
5	1010	85	320	100
6	950	60	430	100
7	830	25	450	100
Av.	916	59	413	100

In a modification³⁰ of this test, the enamel is applied, fired, and then the specimens are pressed together as shown in Figure 121. The two pieces of iron are thereby cemented together by the enamel. When cool the tensile force, required to pull them apart, is determined.

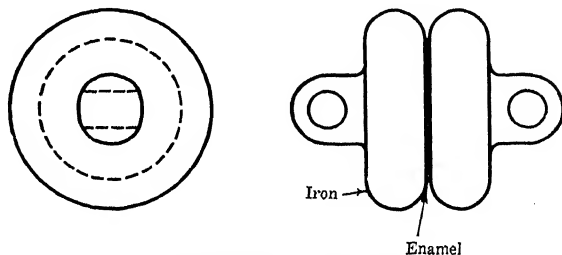


FIGURE 121. Pull Test.

In this test a tensile stress only is applied to the enamel, thus simplifying interpretation; however, the failure generally occurs in the enamel rather than in the bond, thereby it may not be considered strictly as an adherence test.

²⁹ *Ibid.*

³⁰ W. G. Martin, R. R. Roupe, and O. E. Andrus, A. O. Smith, Corp.

HARDNESS

The hardness of enamels does not vary greatly from one composition to another, and there is no satisfactory test for this property.

Mohs' Hardness Test. The most common method of determining this property is that based on the scratch hardness using Mohs' scale of minerals. The test is made by attempting to scratch the enamel surface with samples of minerals of varying degrees of hardness. If the enamel is scratched by a particular mineral, it is softer than that mineral and the next lower in the scale is tried. The highest numbered mineral which will not scratch the enamel is given as the hardness number of the enamel. Vitreous enamels have a hardness between 5 and 6 in the Mohs' scale. Table 50 gives the hardness numbers for Mohs' scale.

Alloy Hardness Scale. Another hardness scratch test based on carbony and steel samples was devised by Navias.* The data on the scratch hardness tests is shown in Table 50.

The use of the Brinell and the Rockwell hardness tests has not proved satisfactory on vitreous enamels.

ELASTICITY

The elasticity of enamel glasses is an important property which has not been extensively investigated. Parmelee and Fetterolf³¹ carried out the most recent work on the elasticity of enamels using simple compositions. The method used and described by them is as follows:

The method made use of an accurately dimensioned glass bar used as a cantilever beam, rigidly fixed at one end and free to deflect at the other upon application of a load. The end of the glass bar was securely fixed in a heavy iron block about five inches square and eight inches in height.

A 500-gram load in every test was applied to the free end of the bar. All bars but two were of such length that the load could be applied at a distance of 20 cm. from the block, making the effective length of the bar 20 cm. This distance was measured as accurately as was possible with a rule marked in tenths of a centimeter. In order to apply the load at the 20 cm. mark a loop of thin wire was passed over the beam at the desired place. A weight attached to the free end of the wire made the effective load 500 grams.

The microscope being focused on the beam at the point where load was to be applied, the bar was deflected several times by pressure from a finger. This was necessary in order to detect any "slack" in the fixed end of the beam. After several repetitions of this treatment, followed by tightening of the cap-screws, the beam returned to its original position after the application of load and could be deflected for an actual measurement.

Preparation of Test Specimens. Test specimens were prepared from cast bars by grinding to accurate dimensions. Owing to the difficulty involved in the method

* Louis Navias, *J. Am. Ceram. Soc.*, 12, 69 (1929).

³¹ C. W. Parmelee and L. D. Fetterolf, *J. Am. Ceram. Soc.* 12, 193, (1929).

TABLE 50. HARDNESS SCALES.*

MOHS' SCALE			CARBOLOY STANDARDS				STEEL STANDARDS				
Material	Hardness	Scratch test	Specimen No.	Brinell hardness (kg./sq. mm.)	Rockwell "A" numbers	Scratch test	Specimen No.	Brinell hardness (kg./sq. mm.)	Rockwell "A" numbers	Scratch test	
Diamond	10		(1)	2000	90		(1)	Stellite	83		
Quartz	9		(2)	1500	87.3	Chemical porcelain	(2)	713	79	{ Spark plug glaze Chemical porcelain glaze (a) Insulator porcelain glaze (b) Chemical glassware Vitreous enamels { Insulator porcelain glaze (b) White earthenware	
			(3)	1400	86.7		(3)	600	75.5		
			(4)	1200	84.3		(4)	477	68		
			(5)		82.8		(5)	387	66		
Feldspar	8		(6)		76.8	Spark plug porcelains { (a) High fire (b) Medium fire (c) Dry process	(6)	340	63		
			(7)			Insulator porcelains { (a) High fire (b) Medium fire (c) Dry process	(7)	286	60		
						Spark plug porcelain glaze					
						{ Chemical porcelain glaze Insulator porcelain glazes (a) and (b) Stoneware Chemical glassware Vitreous enamels					
Quartz	7	{ Spark plug porcelain glaze { Insulator porcelains (a) and (b)	(8)		68.8	White earthenware				Bottle glass	
Feldspar	6	{ Spark plug porcelain { Chemical glassware									
Feldspar	5	{ Vitreous enamels { Insulator porcelain glaze (b) White earthenware									
Quartz	4	Bottle glass									

of casting, the bars were originally of greatly oversize dimensions. These were ground down roughly on a large lap with 60-mesh carborundum and after annealing were again ground in the same manner. Following this, 200-mesh carborundum was used for grinding the beams to the desired size. The use of a small square and a thickness gauge, admirably suited for the work, made possible the preparation of very accurately dimensioned bars. The final polishing was done with 400-mesh carborundum on a smaller lap which had been machined to a true plane surface with special care.

Calculation of Results. The elasticity, E , is given by the equation $E = \frac{4 PL^3}{bd^3 \Delta}$,

in which P is the load, L , the length, b , the width, d , the thickness, and Δ , the deflection.

Accuracy. For substances like glass, there is undoubtedly a large variation in the elasticity among different samples of the same glass. Had it been possible to use more than two specimens of each glass, valuable information might have been obtained on what is known in statistics as normal distribution of values,

TABLE 51
ELASTICITY OF ENAMEL GLASSES

Kg. per sq. millimeter									
Per Cent ZnO replacing Na ₂ O					Per Cent BaO replacing Na ₂ O				
6	12	18	24	30	6	12	18	24	30
4950	5570	5780	5910	6480	5360	5240	5590	5600	5830

standard deviation, and probable error. A large part of the discrepancies which may appear in the results, it is felt, should be ascribed to normal variation among individuals of a population rather than inaccuracy of measurement.

The values for the simple glasses of Parmelee and Fetterolf are shown in Table 51.

It is to be noted that as ZnO replaces Na₂O the modulus of elasticity increases rapidly and quite systematically. In general, replacement of Na₂O and BaO results in a higher modulus, but the effect is much less pronounced than in the case of ZnO. It increased linearly with increasing amounts of MgO and CaO at the expense of Na₂O.

Winkelmann and Schott³² determined elasticity coefficients for glasses by means of a beam of glass suspended at the ends and deflected in the center. Clark and Turner³³ used a rod in place of the beam. C. A. Bell³⁴ used an acoustical method in which the modulus of elasticity was calculated from the frequency of vibration of a glass rod.

H. T. Jessop³⁵ used a method based on the suspension of a beam

³² Jena Glass, Hovestadt (p. 155).

³³ Journal Soc. Glass Tech., III, 260.

³⁴ Phil. Mag., 9, 413.

³⁵ Phil. Mag., 42, 551.

of glass in the center and weighting the ends. The amount of deflection was measured by the interference pattern found by the reflection of light from the bent surface of the beam and a cover glass resting on it.

The factors for calculating elasticity by the equation given on page 40 are compiled in Table 52.

These factors do not agree, probably because of the different types of glass used. The factors F and P^{36} are based on silica as 65 and the factors $*F$ and P^{36} are based on silica as 40. In general, zinc oxide and barium oxide appear to contribute to the elasticity of the glass, especially when substituted for sodium oxide. Parmelee and Shaw³⁷

TABLE 52
FACTORS FOR ELASTICITY

	W. & S. ³⁸	C. & T. ³⁹	F. & P. ³⁶	*F. & P. ³⁶
SiO ₂	65	40	(65)	(40)
Na ₂ O.....	100	110	20, 35	60, 75
BaO.....	100	55	90
ZnO.....	15	80	115
B ₂ O ₃	60
PbO.....
Al ₂ O ₃	150	120
K ₂ O.....	70
CaO.....	70

report that the elasticity increases with a substitution of magnesium oxide and calcium oxide for sodium oxide.

COMPRESSIVE STRENGTH

The compressive strength of enamel glasses is not usually determined, but it is one of the factors entering into its desirable characteristics.

The compressive strengths of enamel glasses were determined by Parmelee and Shaw³⁷ by making glass prisms one centimeter wide and three centimeters tall. These specimens were ground to true dimensions, being especially particular about getting the ends parallel with each other. A special holding device, as shown in Figure 122, was used to eliminate any eccentricity.

The compressive strength varied for the simple enamel glasses from 77 to 81 kg. per square millimeter, the values being about ten per cent below those calculated using Winkelmann and Schott's factors.

³⁶ Fetterolf and Parmelee, J. Am. Ceram. Soc., 12, 193 (1929).

³⁷ C. W. Parmelee and D. T. Shaw, J. Am. Ceram. Soc., 13, 498, (1930).

³⁸ Winkelmann and Schott, Jena Glass by Hovestadt.

³⁹ Clark and Turner, J. Soc. Glass Tech., 3, 260.

TENSILE STRENGTH

The tensile strength of enamels is one of considerable importance, but also one which is extremely difficult to determine because of the brittleness of glass.

Since the investigation which led Winkelmann and Schott to believe that the physical properties of glasses were additive functions of the oxide composition, several researches on the tensile strength have been reported. Winkelmann and Schott⁴¹ used square rods of ten to twenty square millimeters cross section and applied an axial load in two kilogram increments. The load was applied by means of weights which were carefully lowered so as not to jar the glass. The fracture surface was of a dull fibrous appearance over nearly the whole area. The results were quite distinctive, overlapping very little and ranging from 3.28 kilograms per square millimeter for a glass containing 20 per cent silica and 80 per cent lead oxide, to 8.09 kilograms per square millimeter for a glass containing 28 per cent K_2O , 17 per cent ZnO , and 55 per cent SiO_2 .

Griffiths,⁴² working with a single glass:

SiO_2	69.2
K_2O	12.
Na_2O9
Al_2O_3	11.8
CaO	4.5
MnO9

found that the tensile strength of the glass fibers varied inversely as the cross sectional area, from 24,900 pounds per square inch at .04 inches diameter, to 491,000 pounds per square inch at .0013 inches diameter. The tensile strength also varied with (a) maximum temperature, (b) temperature of drawing, (c) presence of impurities or foreign bodies, (d) age of fiber. The strength of a fiber diminished spontaneously for a few hours after preparation to a constant value.

Gehlhoff and Thomas⁴³ state that consistent results were obtained

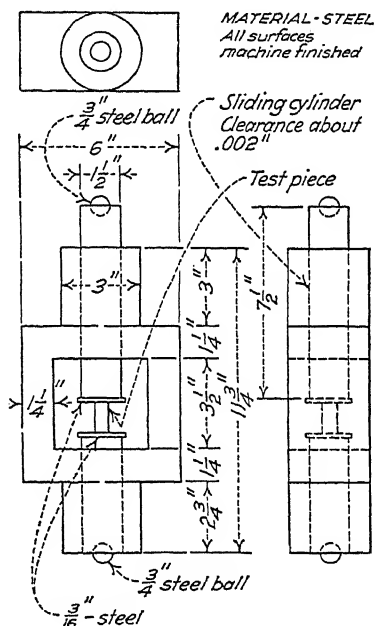


FIGURE 122.
Compressive Strength Apparatus.

⁴¹ Jena Glass, Hovestadt, p. 149.

⁴² J. Soc. Glass. Tech. Abstract 5, 11 (1921).

⁴³ J. Soc. Glass. Tech. Abstract 11, 247 (1927).

by considering that only the fracture area which showed a rough or hackly appearance was broken under tension. They used glass rods about five centimeters long and three to four millimeters in diameter.

Hall ⁴⁴ worked with various base glasses, adding varying amounts of different oxides, and expressed his results as coefficients calculated from the average tensile strength. The results overlapped so much that the drawing of conclusions from the average seems questionable, especially since the maximum result is more likely to be correct. The average tensile strength was found to vary from 11.0 kilograms per square millimeter for a high-soda glass to 34.8 kilograms per square millimeter for a glass high in magnesia and alumina.

A method ⁴⁵ for determining the tensile strength of enamel glasses with a fair degree of accuracy is as follows:

The apparatus consists of two supporting rods, securely and rigidly mounted on a heavy base plate and tied with a heavy crosspiece at the top. From the crosspiece at the top a piano wire hangs with a chuck at the lower end to grip the thread of enamel. At the lower end of the enamel thread an inverted chuck, with another piano wire extending down to the weight can, grips the enamel test thread. Mercury flows into this weight can at a constant rate and is automatically by-passed when the thread breaks. The weights of the can, mercury, and lower chuck together give the weight applied and the cross section of the fractured enamel rod gives the area of the glass. Calculations of the tensile strength are made from this.

The preparation of the enamel specimen is very important, since the results are sensitive to many slight variations in the condition of the specimen.

The enamel to be investigated is milled to pass a No. 60 sieve and then remelted in a platinum crucible and stirred with a platinum rod. After holding for an hour at a temperature slightly below that used for smelting, the temperature of the furnace is lowered until a thread about one millimeter in diameter can be drawn. A long thread of this size is then drawn and broken into pieces about six inches in length. One of these pieces is held in the flame of a bunsen burner and rotated until a slight bead is formed on the end. The specimen is then inverted and slipped into the tapered slot in a plate of iron. The slot must be too small for the bead to pass through, but large enough for the specimen to swing freely. The specimen and iron plate are then held over a bunsen burner so that the other end of the specimen is in the flame and

⁴⁴ J. Am. Ceram. Soc., 13, 182 (1930).

⁴⁵ Method developed by the author with the assistance of R. K. Smith at the University of Illinois. It is similar to the method used at the U. S. Bur. of Stds.

a bead is allowed to form on this end. This bead is regular and straight, since it is formed under the forces of gravity and surface tension. The specimen is then again inverted and the other end held in the flame until the bead has softened and straightened out under the force of gravity. The specimens are next placed in a slotted device and suspended in a small tubular electric furnace. The arrangement of the slots is such that the specimens are left free to shift about and straighten under the attraction of gravity. The temperature of the furnace is then raised just sufficiently to cause the specimen to flow slightly and straighten out, the temperature at which this flow occurs having been previously determined, and then allowed to fall of its own accord, reaching room temperature in about five hours. When cool, one of the specimens is placed in the machine and the mercury receptacle slowly and carefully lowered until its weight is supported by the specimen. The mercury is then allowed to flow into the receptacle from the reservoir. The mercury is kept under a constant head by allowing more to flow in from an upper reservoir as fast as it is withdrawn from the lower. This precaution is taken to assure the same rate of loading for every specimen. As soon as the specimen breaks, the flow of mercury is interrupted by turning off the pinch cock on the connecting tube. The fracture is examined to see if it was broken under pure tension, and the weight of the receptacle and mercury together with that of the lower chuck is taken.

The alignment of the enamel test specimen, the seating in the chuck, freedom from vibration, and controlled cooling are of great importance. The consistency of results should be improved by repeated meltings and grinding of the material to increase its homogeneity.⁴⁶

On eleven tests of a typical sheet iron cobalt ground coat the results of the tensile strength varied only plus or minus ten per cent from the average of about 10 kgm. per sq. millimeter.

ABRASION

The determination of the abrasion resistance of enamels is complicated by the fact that it is very difficult to interpret the results. An enamel in service becomes dirty when the surface gloss is removed by abrasion and, since this gloss layer is extremely thin, a weight loss test cannot be accurately made. This loss of gloss may be produced entirely by the breaking of bubbles in the enamel, the glass between the bubbles retaining its high gloss. This represents an extremely small loss in the weight of the enamel and, if the open bubbles fill with dirt, the sample

⁴⁶ J. T. Littleton, *J. Soc. Glass. Tech.*, 15, 262 (1931).

actually gains in weight. The method of interpreting results based on the appearance is the most promising, but the difficulty of evaluating them is great.

Sand blasting and falling abrasive have been used as tests for abrasion, but they have the objection of being impact tests rather than true abrasion.

The rattler or ball mill test, in which the enameled specimens are milled with the abrasive, also involves considerable impact.

The use of a fixed abrasive wheel to produce the abrasion fails because of the change taking place in the abrasion surface with use.

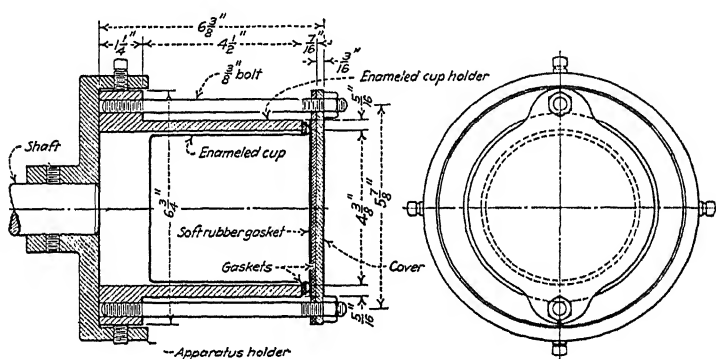


FIGURE 123. Abrasion Apparatus.

Loose abrasive rubbed on the enamel ware changes rapidly in grain size, but does serve as a fair test.

Several methods have been tried, in which the sample is revolved in the abrasive, but no standard test has yet been adopted.

C. J. Kinzie⁴⁷ devised a method in which a one-quart cylindrical enameled cup containing the abrasive materials was rotated at 63 rpm for forty-one hours. The materials used for the abrasive varied from washing powder to sand and porcelain balls. The cup was weighed before and after each run, the loss in weight representing the amount of abrasion. The apparatus used and the dimensions of the cup are shown in Figure 123. The loss in weight of the cups varied from .3 to .7 of a gram and could be duplicated fairly accurately.

A test devised in the author's laboratory and showing promise consists in rotating a twenty-four inch metal-clad wooden disk with the lower half in a box of abrasive. The flat test specimens are fastened on the sides of the disk, thus being carried through the abrasive. Stan-

⁴⁷ C. J. Kinzie, *J. Am. Ceram. Soc.*, 12, 188-92 (1929).

standard ten-mesh carborundum is used as the abrasive and the test consists of running the specimens for 10,000 revolutions at a speed of 320 rpm.

The interpretation of the results in terms of loss in weight was unsuccessful, but, by setting up a series of standards for comparison, duplicate results could be obtained.

DENSITY

The specific gravity of enamel glass can best be determined by use of a specific gravity bottle. About ten grams of the enamel glass passing a No. 100 sieve are dried at 100° C and placed in a glass-stoppered weighing bottle. About two grams of this dry enamel powder are accurately weighed into a previously weighed pycnometer. Previously boiled water is added to about two-thirds full and the sample agitated to eliminate any entrapped bubbles of air. The bottle is then filled to the top and brought to a temperature of 20° C \pm 1° C. The bottle is wiped dry and weighed.

Calculation. The following formula should be used:

$$S = \frac{w - p}{(w - p) - (w_2 - w_1)}$$

in which S = the specific gravity of the enamel

w = weight of the stoppered pycnometer and sample

w_1 = weight of stoppered pycnometer filled with water only

w_2 = weight of stoppered pycnometer, sample, and water

p = weight of stoppered pycnometer

DANIELSON-LINDEMANN DEFLECTION TEST

The deflection of enameled iron strips has become a fairly common test for the comparison of enamels and is used in some plants for control.

The test was originally devised by R. R. Danielson and W. E. Lindemann,⁴⁸ but was later studied by many investigators.

The tentative method of the American Ceramic Society for the determination of the resistance of sheet-iron enamel to deflection is as follows:⁴⁹

Testing Machine. The machine used in the test shall embody the essential details of that shown in Figure 124.

⁴⁸ J. Am. Ceram. Soc., 8, 795 (1925).

⁴⁹ Report of the Enamel Division Standards Committee 1930, Bull. Am. Ceram. Soc., 9, 269 (1930); Bull. Amer. Ceram. Soc., 7, 362 (1928).

Preparation of Test Pieces. The metal base should be strips from 22-gauge enameling stock, cut 2 inches wide and 12 inches long. For convenience in handling during processing, a $\frac{1}{4}$ -inch hole may be punched near one end of the strip.

The numbered strips should be carefully pickled and, after drying, weighed to the nearest $\frac{1}{2}$ gram and calipered to the nearest 0.001 inch. They should be dipped in commercial ground coat, dried, fired, weighed, and calipered. Strips which do not appear to represent good local practice should be rejected. Two coats of the enamel to be tested should be applied. Before firing each cover coat, the edges should be brushed back $\frac{1}{8}$ inch to prevent the formation of a bead. Pieces showing excessive warpage or having firing tool marks near the center should be rejected. After enameling, the strips should again be weighed and calipered as before, and by subtracting the weight and thickness in ground coat, the weight and thickness of the cover enamel are determined. For use in the test only strips bearing cover enamel within $\pm \frac{1}{2}$ gram and ± 0.001 inch of the amount determined upon should be used.

Testing. With the center roller dropped to a sufficiently low position, test pieces should be so placed in the machine that the back ends will rest against the under side of the back roller, with the front ends not touching the front roller. The position of the center roller should then be advanced until one or more of the strips just touches the under side of the front roller. The dial should be read and this reading taken as the initial reading for the strips thus making contact. The center roller should then be advanced at the specified rate and the dial readings taken where each of the other strips makes contact.

From the time that the first strip makes contact until the last strip has failed, the center roller should be advanced at the uniform rate of 0.02 inches every two minutes.

After the last strip has made contact the surface of each piece over the center roller should be coated with a smear of lampblack in vaseline, and just before each advance in position, the surface should be rubbed carefully with a cloth to note whether or not a crack has been produced. Care should be taken to confine this rubbing to the area immediately over the center roller, otherwise pressure on the test pieces may affect results.

When the first significant crack appears on a given strip, the dial should be read and the value recorded as the final reading for the strip involved. (The term "significant crack" should be taken to mean a crack extending more than half-way across the test piece.)

The difference between the initial and final readings for a given strip, expressing the number of hundredths of an inch of deflection to produce failure, should be taken as the deflection value for the piece.

Deflection Value. The deflection value for a given enamel should be the average results from not less than six individual test pieces. The record of the test should include the average weight and thickness of the ground and cover coats.

Note 1: In addition to the information afforded by the deflection to produce first crack, it is of value to continue the advance of the second roller, noting the behavior of the enamel under the more extreme deflection.

Note 2: Two procedures are recognized as being available, depending on whether the test is being used in connection with shop control or with development research.

(A) In shop control, it is recommended that each shop determine the weight and thickness of enamel on the standard piece corresponding to the thickness used in commercial practice, and that this weight and thickness be adhered to in the preparation of test pieces. (Information now available suggests a weight range of from 7 to 10 grams as covering practice for two coats of white enamel.)

(B) In connection with development research, where more complete information is desirable, it is recommended that for each enamel there be prepared test pieces of three or more different thicknesses, covering a range from well below to well above the normal thickness. The average deflection of each set plotted against the corresponding thicknesses results in a curve which affords a truer picture of the behavior of the enamel than does a determination on only one thickness.

CHEMICAL PROPERTIES

The chemical properties of enamels vary over a wide range. Some enamels will withstand strong acids for long periods of time and at elevated temperatures, while others are stained by water at room temperatures. Again the principle of sacrificing one property to develop another more important to a particular use comes into effect. If high resistance to solubility is desired, the low fusibility must be sacrificed and, if high resistance to acid is desired, high resistance to alkali must be sacrificed. A practical compromise is generally reached, however, wherein the properties are balanced to suit the service conditions of the enamel.

The chemical properties are important to enamels used for industrial tanks, kitchen ware, or any other ware where the enamel is subjected to acid or basic solutions. Chemical resistance is also necessary in enamels used for signs or other purposes, where they are subjected to weather conditions. The corrosion resistance of enamels also finds an important place in pipe and equipment buried in the soil.

Only acid-resisting enamels can be used for food utensils, particularly if the enamels contain either lead or antimony. Lead should not be present (is practically never present) in such enamels and care must be taken if antimony is used. The antimony in enamels is added as an opacifier and since only that oxidized to the pentoxide contributes opacity most of it is inert.

Under ordinary food service the antimony is not detrimental because the enamel, even when soluble, dissolves only very slowly and most of the antimony when present is in the inert form and even then in very small amounts. If, however, antimony enamels which are soluble in fruit acids, such as strong lemon juice, are used, there appears to be a possibility of difficulty. No such cases in America are known to the author, but a few rare cases of temporary illness have

been blamed on enamel in Europe.⁵¹ The theory of these cases is that the trivalent antimony reacted with citric or tartaric acids in strong lemon juice when the enamel, which must have been of exceptionally poor quality, was dissolved.

The simple spot test (page 369), using lemon juice, should be an assurance against any possibility of trouble. This spot test is commonly used by manufacturers of enameled ware, in routine proving of their quality.

The mechanism of solution is not the same with all enamels. Some enamels are etched uniformly over the surface, some quite unevenly, and others only in lines between what appears to be grains of insoluble enamel. The first type of solubility is characteristic of enamels which show only moderate resistance. The second type with irregular attack is characteristic of enamels which are improperly processed, while the third type, showing line or grain inter-face attack, is characteristic of acid-resisting, but not acid-proof enamels. This last type of attack can be halted by refiring, as explained on page 348.

ACID TESTS

Four different acid tests are in common use, the spot test, the grain test, the dish test, and the reflux test.

Spot Test. The simplest acid test for enamels is the spot test. It consists of placing a drop of acid solution on the ware for a given period of time, washing, and observing the effect. This test is very sensitive, enamels being generally attacked in five minutes, if they are at all soluble in the solution. It is a simulative service test for many types of ware, such as kitchen sinks, table tops, and refrigerator linings. A test of this sort, using ten per cent citric acid placed on the enamel for fifteen minutes, will usually show a stain, unless the enamel is very resistant to fruit juices and weak acids.

Grain Test. The grain test consists of subjecting grains of frit of known size to acid solution (usually at an elevated temperature) for a definite period of time.

A convenient grain test is one in which frit, passing a No. 20 sieve and remaining on a No. 30 sieve, is first washed with absolute alcohol to remove any adhering dust. Ten grams of the frit are then weighed into a 150 cc. Erlenmeyer flask, to which are added 75 cc. of a twenty per cent solution of hydrochloric acid. The flask is stoppered with a cork through which a five millimeter glass tube extends about twenty

⁵¹ G. W. Monier-Williams, Reports on Public Health and Medical Subjects, Ministry of Health, No. 29 (1925), No. 78 (1934).

centimeters above the flask to act as a reflux condenser. The flask is then placed on a sand bath and the contents boiled for five hours. Since a twenty per cent solution of hydrochloric acid is about a constant boiling proportion, the acid automatically stays at this concentration throughout the test.

After the heating period the residue is washed onto a previously prepared, dried, and weighed Gooch filter. The residue is then dried and weighed. The following formula gives the percentage loss in weight of the enamel:

$$\text{Percentage Loss (solubility)} = \frac{\text{Wt. of sample} - \text{Wt. of residue}}{\text{Wt. of sample}} \times 100$$

Dish Test. The dish test consists of placing an acid solution in a previously weighed, enameled dish and determining the loss of weight over a period of time. This test has many modifications with respect to the strength and composition of the acid solution and the temperature and time used. In some cases, the results are represented as a loss in weight and in others by the appearance. The use of dyes or "aquadag" on the attacked surface sometimes aids in the interpretation of results by visual inspection.

Reflux Test. The typical reflux test is confined chiefly to tests of highly resistant enamels. In this test a water-cooled reflux condenser is used on a receptacle, either lined with the enamel to be tested or containing the enameled test piece. The acid solution is boiled in this receptacle, the enamel being thereby tested in either the liquid or the vapor phase or both. The results are expressed either on the basis of appearance or as loss in weight.

ALKALI TESTS

The tests for resistance to alkali are carried out in a similar manner to those for acid, except that an alkaline solution is used. Alkali attack is generally slower than acid attack; therefore the use of the spot test is not common.

HOT WATER TEST

Water at temperatures up to the boiling point does not affect most enamels, even in extremely long periods of time. The reflux boiling test is, therefore, only used if the enamels are quite soluble.

AUTOCLAVE TEST

At temperatures above boiling, many enamels are rapidly disintegrated by the action of either the steam or the water phase, the former being much more severe.

In the autoclave test, the enamel specimens and water are placed in an autoclave (steam-tight cylinder or bomb) and heated above the boiling temperature of water. The temperature and the pressure rise together, either being useful for the measurement of the conditions. Most enamels, exposed to pressures of 48 lbs. (295.5° F) show attack in twenty-four hours. The attack increases with time. Some enamels will withstand 190 lbs. (383.7° F) for several days, but, as time passes, the enamel will be completely removed from the iron.

TABLE 53
TEMPERATURE AND GAUGE PRESSURE RELATIONS IN AN AUTOCLAVE

	<i>Pressure in pounds</i>		<i>°F</i>	<i>°C</i>
Atmosphere.....	0	212	100	
Steam.....	25	266.7	130.4	
Steam.....	50	297.7	147.6	
Steam.....	100	337.3	169.9	
Steam.....	150	365.9	185.8	
Steam.....	200	387.9	197.7	
Steam.....	250	406	207.8	

WEATHERING

Many enamels are severely attacked by outdoor weather conditions. This attack is often called fading because of the change in color, but is actually a solution of the enamel surface. It is particularly severe in congested areas where the atmosphere contains sulphur gases and carbon dioxide. It is bad in seacoast towns where the humidity is high. In some cases, enamels show a similar condition caused by heavy dust and sand blown against them. Enamels used for signs or other outdoor service are usually very resistant to solution.

No satisfactory test for the weather resistance of vitreous enamels has been devised and no survey of the different types of enamels exposed to actual service conditions has ever been completed. The present sign enamels are a result of interpretations from acid tests and a survival of the fittest.

The weatherometer, designed and used for studying the resistance of paints to weather, has not been particularly successful for vitreous enamels.

EFFECT OF SOIL

The effect of soil on enamels opens an important and large field for the use of vitreous enamels in the prevention of corrosion. The work on this subject has, however, been limited to a few companies⁵⁰ that are particularly interested and the exact information is not

⁵⁰ A. O. Smith Corporation, Milwaukee, Wisconsin.

available for publication. Enamels can, however, be made resistant to many years of exposure in both acid and basic soils. Reports on enamel ware buried for many years are available.

An accelerated soil test can be used to compare enamels for this purpose. The autoclave test, the acid test, and the alkali tests are not reliable as a means of determining resistance to the action of soil.

SCUMMING

The scumming of enamels caused by sulphur gases during manufacture can be identified by the salty taste. If the scum is dissolved off the enamel with distilled water and treated with a few drops of barium chloride solution, a white precipitate of barium sulphate forms.

CHEMICAL ANALYSIS

The chemical analysis of enamel glasses is a highly specialized branch of analytical chemistry and will not be described here. The separation, of the elements present, is difficult and should be entrusted only to a skilled analyst who is familiar with this type of work.

DEFECTS

Although an enamel may be made under conditions which are carefully controlled, occasional defects will appear. The tracing of defects to their source and the elimination is often very troublesome. It is quite common for a defect to be the result of several contributing factors, none of which alone would cause it. It is far easier to avoid defects than it is to eliminate them.

Blistering. Blistering is the existence of gas bubbles in the surface of the cooled enamel.

In the firing of enamels, gases are evolved which must escape through the surface. In some cases the volume is large and the time of evolution is long, while in other cases the effect is hardly perceptible. To avoid blistering, these gases must escape and the enamel must heal over.

If the iron is poor, high in carbon, or not properly cleaned and prepared for the enamel, the evolution of gases is either excessive or the bubbles are so large that they cannot be eliminated. Improper preparation of the metal surface is the most common cause of blistering and the one which is first suspected.

Since bubbles of gas must pass through the enamel to escape during firing, any factor contributing to an increased viscosity or surface

tension of the enamel will contribute to the entrapping of these gases. Thus, underfiring with regard to either time or temperature is a cause for blistering. If the enamel coating is unduly thick, it may in itself prevent the rapid elimination of the gases.

Water vapor in the atmosphere of the furnace during firing will also cause severe blistering, although the exact reason for this is not known.

Any dirt or impurities in the enamel may cause an increased evolution of gas and result in blistering.

In summarizing, blistering may be caused by (a) improperly cleaned iron, (b) poor iron, (c) improper firing, (d) thick application, (e) contamination by impurities, and (f) water vapor in the furnace atmosphere.

Chipping. Chipping is the cracking off of pieces of enamel either during the cooling or later. Chipping usually extends to the iron, although in some cases it does not.

Given a good enamel, chipping is generally caused by too thick a coating, mechanical abuse, or a dirty metal surface. If the enamel has a smaller thermal expansion than the iron, the tendency for chipping is aggravated. The enamel, on cooling from the furnace temperature, is thus put under compression by the iron and chipping results. Wherever enamel collects as a bead or gob, chipping is likely to occur, because of the uneven strains set up. At sharp corners or edges chipping is quite common, therefore, these should be avoided in the design of the ware.

In the assembly of enameled parts mechanical abuse is a common cause of chipping. The cover enamels are not often used around screw holes, since the additional thickness of these coats aggravates chipping at such places where the enamel is subjected to strain.

Copper-heading. Copper-heads are reddish brown spots which appear in sheet iron ground coat enamels. These spots may vary in size from almost invisible specks to about one-eighth of an inch in diameter. The small copper-heads are always depressed, but the large ones may be accompanied by a pulling away or curling up of the enamel.

On examining copper-heads under a microscope by both cross-section and vertical view, they appear to be of a slag-like nature. In most cases they extend from the iron to the enamel surface. They appear to be caused by the oxidation of the iron due to a break in the continuity of the enamel or a floating of iron scale or oxide in the enamel.

Copper-heads are generally caused by either badly boiling iron or a surface which has not been properly prepared for enameling. If the iron boils badly, little can be done to eliminate copper-heading, although very fusible enamels fired at lower temperatures are more successful than the harder ones. Irons having a high carbon content tend to copper-head more than those of low carbon. If sheet iron is blasted with steel grit, copper-heading is quite prevalent. High-pressure sand blasting also aggravates copper-heading.

Improper cleaning and pickling of the iron may cause copper-heading, due to the fact that the enamel does not adhere well to dirty iron and may, therefore, allow air to get to the iron. The elimination of dirt on the iron surface may cause large bubbles, which on breaking allow the oxygen of the air to reach the bare metal and start copper-heading.

Copper-heading is more likely to occur if the enamel is too thin, because of the ease of slagging through the thin surface.

Crazing. Crazing is a cracking of the enamel coating into a net work of very fine lines. The cracks extend from the surface of the enamel to the iron and may be straight or irregular. Crazing occurs after the enamel is cooled or in alternate heating and cooling in use. It is caused by uneven expansion and contraction of the enamel and the iron. The proper adjustment of the enamel composition, the elimination of the severe heating and cooling of the enamel parts in service, and proper design are about the only methods of avoiding crazing.

Egg Shell. An egg shell appearance of the surface is caused by many small bubbles bursting at the surface of the enamel when it cools. It is usually characteristic of the enamel composition, although moisture in the furnace atmosphere may contribute.

An enamel high in the alkalies (sodium and potassium) is very likely to show the egg shell appearance. Over twenty per cent of alkalies in the total chemical composition is dangerous. A high fluor-spar cover enamel also tends to egg shell; in fact an excessive amount of any of the most volatile fluxes tends to develop this defect. Some clays used as mill additions produce a similar effect.

Fishscale. Fishscales in enamel are small chips or scales which pop loose from the layer after the enamel is cooled. They may appear immediately or they may be delayed for some time. Two varieties are recognized—the fine fishscale “shiners” and the large fishscale. These particles are half-moon shaped, thin on one edge and thick on the other, resembling the scale on fish.

Fishscale is a defect occurring only in sheet iron ground coats, although in some cases the fishscale is delayed until after the cover

enamel is applied, in which case the defect extends through the cover enamel. It is, therefore, not uncommon to see fishscale in cover enamels, but these fishscales are believed always to find their source in the ground coat.

Fishscaling is one of the very troublesome defects occurring in enamels, because the source is often very difficult to trace. It seems to be caused by many conditions, and often combinations of these conditions, none of which would cause it alone. In the elimination of fishscale it is necessary to check up on the control of the enamel through the entire manufacturing process, raising the standard of quality throughout.

The composition of the enamel influences the fishscaling tendency in that it controls certain physical properties such as thermal expansion, strength, and elasticity. Some compositions are much more likely to fishscale than others, but any ground coat may fishscale if other conditions contribute to it.

If the enamel is under-smelted, it is likely to fishscale because of the non-uniformity of the glass and, if over-smelted, it is likely to fishscale because of the loss of fluxes and the development of a weak, brittle glass.

Milling of the enamel may offer a source of contamination of mill lining or balls, which may cause fishscale. Irregular sized particles in milling also contribute to an uneven enamel glass after firing. Mill additions affect the set of the enamel and may, therefore, indirectly cause fishscaling. An enamel which is not properly set up is quite likely to segregate, which again contributes to the strains in the fired enamel and results in fishscale.

The application of enamel to give a uniform coating of glass is important. Dip tanks which are not thoroughly stirred or contain considerable residue are likely to contribute to the fishscale defect.

Poorly prepared enameling surfaces cause an uneven adherence and distribution of strains in the enamel and may cause fishscale. The cleaning and pickling of the iron is, therefore, a factor of importance.

Underfired enamels are weak mechanically and have not been melted to a condition of uniformity. Fishscales caused by underfiring are of the large variety, which are often delayed until after the ware has passed inspection.

Fishscales caused by overfiring are of the small, or shiner, variety. They may be almost microscopic, appearing to the naked eye like tiny stars. They are probably due to the volatilization of some of the fluxes

at the surface, the concentration of fluxes at the surface, or the elimination of too great an amount of the bubble structure of the enamel.

To fire enamels successfully without producing fishscale, it is necessary, therefore, to watch the temperature distribution and any change in the equipment that may influence this.

The base metal is another important source of fishscale, particularly if the carbon content, thermal expansion, or thickness is not uniform. The enamel may fit one iron and never fishscale, while with another one it may fishscale badly.

Insufficient oxygen to produce good adherence may induce fishscale, which usually appears first as light spots under the surface, but which later breaks through.

Gloss. The quality of the gloss of enamels is the result of many factors. The chemical composition must be controlled to avoid pin-hole bubbles, devitrification and scumming, which are detrimental to gloss. Excessive mill additions or mill additions that contribute impurities which form scum or excessive gassing must be avoided.

Underfiring is a common cause of poor gloss, while improper firing of any kind, smelting, or milling may contribute appreciably to the defect.

Hairlining. Hairlining differs from crazing in that the cracks are healed over in subsequent firings. They are characteristic of sheet iron ground coats, although they also occur in wet process cast iron enamels. Hairlining usually makes up a more or less regular pattern, the lines radiating from a certain area or running parallel.

Hairlining may be caused by strains due to design, mechanical abuse, unequal heating and cooling, or underfiring. The design of corners, flanges, ears, or handles may be a contributing cause of hairlining. For example, this defect often appears on kitchen ware near the handles, on table tops near the edges, or stove parts near the flanges. Mechanical strains produced by rough handling or bending the ware after removing the ground coat from the furnace are a common cause of hairlining. In the brushing operation, the ware should be kept flat and placed on a solid base so that it will not be excessively distorted.

Unequal heating or cooling may cause strains leading to hairlining. If the ware is crowded in the furnace, it is not uniformly heated and unequal firing or underfiring of certain areas is the result.

In cast iron ware hairlining is usually caused by poorly designed castings with unequal thicknesses. The latter is not common, however,

and hairlining is characteristically a sheet iron ground coat defect which appears in the subsequent coats of enamel.

Jumping. Jumping is a chipping of the first coat during the subsequent heatings of the cover enamels. It is caused by poor adherence to the iron, which permits the ground coat to pop off, taking the cover enamel with it, when subjected to the strains of reheating. It is more characteristic of wet process cast iron enamels than sheet iron, but does occur with both.

The fundamental cause of jumping is iron which is not perfectly clean. A spot of oil, scale, rust, or dirt may prevent the ground coat from adhering in that area. The coating, therefore, readily shatters when subjected to reheating and the iron is left bare. Jumping can sometimes be traced to rust spots which formed even before thorough sandblasting on cast iron.

Tool Marks. Tool or pin marks are cracks radiating from the point where the ware rested on the tool during firing. They are generally caused by either too heavy tools or tools which are too cold. The difference in the rate of heating or cooling around these points causes the metal to strain or bulge, resulting in the cracks in the enamel.

Reboiling. When the cover enamel is fired over a ground coat on sheet iron, the ground coat sometimes boils at about 1100° F, causing breaks in the continuity of the cover enamel. This defect appears in the cover enamel as dark specks where the ground coat enamel has pushed up through the cover. The exact causes and remedies are not known although the defect is more common with some irons than with others. See page 297.

Rusting. During the drying of ground coat enamels, rust is sometimes formed, which causes a discoloration. It is more common on cast iron enamels, of both the wet and dry process, than in sheet iron enamels. Rusting nearly always takes place in drying the slush coat on dry process enamels, but, since it is not objectionable unless very bad, it has not received much attention there. In sheet iron ground coats rusting is not common, since a choice of electrolytes can be made to control it. The use of magnesium sulphate for such enamels promotes rusting and should be avoided. Sodium nitrite, ammonium carbonate and sodium carbonate tend to inhibit rusting in sheet iron ground coats. The nature of the steel influences the extent and nature of the rusting, a commercially pure iron rusting very little, while an impure or high carbon iron promotes rusting.

Rusting is sometimes quite troublesome in wet process cast iron enamels; the nature of the enamel itself seems to influence the effect of

the particular electrolyte. The common inhibitors which prevent it in one case may not function in another; therefore, trial tests with these different salts constitute the most dependable method of securing an enamel which does not cause rusting of the iron.

In any case of rusting, rapid drying is the most desirable procedure, since such treatment reduces the length of time during which rusting can take place. Where rusting is desired, as in granite ware, humidity dryers are used to lengthen the rusting period.

Specking. Specking is the occurrence of dark specks in light enamel. It is generally caused by contamination from foreign materials, although it may be due to reboiling, or even fishscaling. Sometimes the latter two causes can be identified by underfiring a piece of ware and observing the specks. If due to fishscale, they are easily recognized and, if caused by reboiling, the bubbles should be perceptible.

Foreign material in an enamel may find its source either in the raw materials or from any of the manufacturing operations. To trace the source of this material, it is usually necessary to check up on all of the operations with the elimination of dirt in general. Much could be written on this subject, since there are many places where foreign materials may enter the enamel.

Tearing. Tearing generally appears in the firing process, although it finds its source in drying. The enamel cracks in drying and pulls away along irregular tears, exposing the enamel underneath. Sometimes it extends clear through the coat and sometimes it is merely a surface defect. When the whole enamel layer pulls away, it is sometimes the cause of crawling and curling. It is essentially a cover enamel defect, although in some cases it does occur in ground coats.

The common causes of tearing are too fine grinding or too rapid drying. The enamel shrinks during the drying process; therefore anything which either increases the total shrinkage or decreases its drying strength is likely to promote tearing. Fine grinding increases the amount of shrinkage because of the fineness of the particles, and the necessity for additional water in the slip to make it apply well. If applied too wet or dried too rapidly, the enamel surface dries before that underneath and a differential shrinkage is produced, which results in drying cracks. Too heavy an application causes the same effect and is a common cause for tearing, even if all other conditions are satisfactory. If the clay content is low, the strength of the dry coating decreases and tearing is likely to occur.

Some enamel compositions tear much more than others; for example, those high in boric oxide or those of high acid resistance are

more likely to tear. Such enamels must be milled more coarsely and additional clay and electrolytes may be necessary.

Warping. Warping is the distortion of the ware during firing or on cooling. The most common cause of warping is poor design or improper support during firing. Light gauges of metal must be supported at more places than heavy stock to prevent sagging between the supports. Such trouble is readily detected and remedied. In some cases the design of the ware is such that it heats and cools unevenly or does not have sufficient strength to support itself. In the former case the design must be either modified or the arrangement in the furnace changed to take care of the differences in temperature. In the latter case it may be necessary either to change the design, to brace the ware, or to use a heavier gauge stock.

If the enamel composition is such that its thermal expansion is not close to that of the metal, it may cause warping, even of flat sheets hung vertically.

In some cases strains within the metal may cause warping, and an annealing operation will be necessary to eliminate the trouble.

Wavy Surface. A wavy surface on an enamel is generally caused by uneven application or a rough iron surface. Enamels which are very viscous tend to fire with a wavy surface, if they are not applied smoothly. Dry process enamel milled too fine for the dredge used in dusting will often cause a wavy appearance, due to uneven application. Although wavy appearance often passes inspection, it should be avoided, because it detracts markedly from the quality of the ware.

DRY PROCESS CAST IRON ENAMEL DEFECTS

The following is a description ⁵² of the defects characteristic of dry process cast iron enamels in particular:

Run-Down, Beading. A *run-down* is an excessive amount of gloss coat gathering in one place on the ware. When a run-down occurs on the edges of the ware, it forms into beads and is known as *beading*. Ordinarily it takes only a slight blow on such a bead to cause chipping. This type of chip cannot be distinguished from the ordinary edge chip caused by a blow, unless the bead is seen before or after the damage occurs. A run-down and liver along a bevel or corner of the apron very seldom chips off, unless the blow is severe enough to chip the ordinary enameled surface. When the run-down occurs on the inside of the ware at the bottom corners, it sometimes results in a craze and may be distinguished as such. Unless the run-down, or liver, is of

⁵² American Railway Assoc. Freight Container Bureau Bul. No. 27.

large size and prominent, the manufacturers do not consider it a cause for rejection.

Casting Crack. A casting crack is a crack with no chipping around it. It is usually a manufacturers' defect rather than a handling damage, for in the latter case there is, as a rule, considerable chipping around the damaged portion of the casting. Sometimes, however, there is chipping around a defective casting crack, and to ascertain whether or not the chipping and crack were caused by a defective casting or by handling, the casting itself must be examined closely. If the casting is defective, a small amount of the ground coat or the paint on the back of the casting will have run into the crack and adhered there, whereas, if the casting has been broken by handling, the crack will be perfectly clean.

Crazing. Crazing is usually due to an over-thickness of iron in the casting or to an over-thickness of the enamel coat at the point where the crazing occurs. During the firing an unequal expansion of the enamel coat and the casting occurs at such points and, upon cooling, unequal stresses are set up in the enamel and casting, resulting in the hairline cracks. This type of defect is most prevalent along corners of the ware. It can be distinguished from the handling damage (shatter) caused by a blow on the casting, in that the lines of a craze will be nearly parallel, while the lines of the cracked enamel of a shatter will normally intersect or radiate from the central point where the blow was struck.

Peeling (Lift). Peeling is caused by a number of faults in the manufacturing process, among which are the overfiring or underfiring of the ground coat, the casting not having been thoroughly cleaned before the ground coat was applied, or the ground coat having been rubbed off in places before the gloss coat was applied. Any one of these faults will contribute to the conditions shown. Peeling is prevalent at the free end of the apron of a bath tub, not protected during the firing by the body of the tub, and at points where there is a pronounced bevel. This type of defect can be distinguished from the handling damage (chipping) by the fact that the edges of the broken enamel will be more or less perpendicular to the surface of the casting and the outline of the break will not have an irregular and shattered appearance, while in chipping the edges of the break will have a shattered appearance and usually will be tapered away from the surface of the casting.

Pin Hole Blister. A pin hole is a blister in the enamel coat which has burst during the firing process, allowing the enamel to run down the hole and leave a wavy effect. The blister in the enamel may result

from several different causes, the principal ones being imbedding of carbon particles in the gloss coat, a slight pit or hole in the casting itself, and foreign matter in the metal of the casting. Any one of these faults causes gases to be released under the surface of the enamel while the ware is being fired. The gas expands and forms a small bubble or blister. This bubble may burst during the firing process and allow the enamel to run down in the small hole formed, leaving the surface wavy. When this occurs, the defect is a pin hole. If the bubble does not burst during the firing, the defect is a blister.

Pop-Off. A pop-off consists usually of a small portion of the enamel separating from the casting, the broken piece being tapered from the surface, leaving a small crater-like hole with the apex at the casting. This defect may be due to a number of causes, the principal ones being a small pit in the casting, or foreign matter other than iron in the casting. A pop-off may also be caused by foreign matter becoming imbedded in the enamel and in this case the break in the enamel seldom extends to the casting.

APPENDIX

TABLE 54
INTERNATIONAL ATOMIC WEIGHTS (1933)

<i>Name</i>	<i>Symbol</i>	<i>M</i>	<i>Name</i>	<i>Symbol</i>	<i>M</i>
Aluminum.....	Al	26.97	Molybdenum.....	Mo	96.0
Antimony.....	Sb	121.76	Neodymium.....	Nd	144.27
Argon.....	A (Ar)	39.944	Neon.....	Ne	20.183
Arsenic.....	As	74.93	Nickel.....	Ni	58.69
Barium.....	Ba	137.36	Niobium.....	Nb	93.1
Beryllium.....	Be	9.02	Nitrogen.....	N	14.008
Bismuth.....	Bi	209.00	Osmium.....	Os	190.8
Boron.....	B	10.82	Oxygen.....	O	16.000
Bromine.....	Br	79.916	Palladium.....	Pd	106.7
Cadmium.....	Cd	112.41	Phosphorus.....	P	31.02
Cesium.....	Cs	132.81	Platinum.....	Pt	195.23
Calcium.....	Ca	40.08	Potassium.....	K	39.10
Carbon.....	C	12.00	Praseodymium.....	Pr	140.97
Cerium.....	Ce	140.13	Radium.....	Ra	225.97
Chlorine.....	Cl	35.457	Radon.....	Rn	222.00
Chromium.....	Cr	52.01	Rhenium.....	Re	186.31
Cobalt.....	Co	58.94	Rhodium.....	Rh	102.91
Columbium.....	Cb	93.3	Rubidium.....	Rb	85.44
Copper.....	Cu	63.57	Ruthenium.....	Ru	101.7
Dysprosium.....	Dy	162.46	Samarium.....	Sm	150.43
Erbium.....	Er	167.64	Scandium.....	Sc	45.10
Europium.....	Eu	152.0	Selenium.....	Se	79.2
Fluorine.....	F	19.00	Silicon.....	Si	28.06
Gadolinium.....	Gd	157.3	Silver.....	Ag	107.880
Gallium.....	Ga	69.72	Sodium.....	Na	22.997
Germanium.....	Ge	72.60	Strontium.....	Sr	87.63
Gold.....	Au	197.2	Sulphur.....	S	32.06
Hafnium (Celtium)	Hf	178.6	Tantalum.....	Ta	181.4
Helium.....	He	4.002	Tellurium.....	Te	127.5
Holmium.....	Ho	163.5	Terbium.....	Tb	159.2
Hydrogen.....	H	1.0078	Thallium.....	Tl	204.39
Illinium.....	Il		Thorium.....	Th	232.12
Indium.....	In	114.8	Thulium.....	Tm	169.4
Iodine.....	I	126.92	Tin.....	Sn	118.70
Iridium.....	Ir	193.1	Titanium.....	Ti	47.90
Iron.....	Fe	55.84	Tungsten.....	W	184.0
Krypton.....	Kr	83.7	Uranium.....	U	238.14
Lanthanum.....	La	138.92	Vanadium.....	V	50.95
Lead.....	Pb	207.22	Xenon.....	Xe	131.3
Lithium.....	Li	6.940	Ytterbium.....	Yb	173.5
Lutecium.....	Lu	175.0	Yttrium.....	Y	88.92
Magnesium.....	Mg	24.32	Zinc.....	Zn	65.38
Manganese.....	Mn	54.93	Zirconium.....	Zr	91.22
Mercury.....	Hg	200.61			

STANDARD SCALES FOR TESTING SIEVES *

(A) U. S. Standard Sieve Series †

This sieve scale is essentially metric. The sieve having an opening of 1 mm. is the basic one, and the sieves above and below this in the series are related to it by using the fourth root of 2, or 1.1892 as the ratio of the width of one opening to the next smaller opening. In making selections from this series it is recommended that this be done on some systematic plan, as for example, the selection of every other sieve or of every fourth one in the series.

TABLE 55

<i>Mesher per lineal inch</i>	<i>Sieve number</i>	<i>Sieve opening (inches)</i>	<i>Sieve opening (millimeters)</i>	<i>Wire diameter (inches)</i>	<i>Wire diameter (millimeters)</i>
2.58	2½	.315	8.00	.073	1.85
3.03	3	.265	6.73	.065	1.65
3.57	3½	.223	5.66	.057	1.45
4.22	4	.187	4.76	.050	1.27
4.98	5	.157	4.00	.044	1.12
5.81	6	.132	3.36	.040	1.02
6.80	7	.111	2.83	.036	.92
7.89	8	.0937	2.38	.0331	.84
9.21	10	.0787	2.00	.0299	.76
10.72	12	.0661	1.68	.0272	.69
12.58	14	.0555	1.41	.0240	.61
14.66	16	.0469	1.19	.0213	.54
17.15	18	.0394	1.00	.0189	.48
20.16	20	.0331	.84	.0165	.42
23.47	25	.0280	.71	.0146	.37
27.62	30	.0232	.59	.0130	.33
32.15	35	.0197	.50	.0114	.29
38.02	40	.0165	.42	.0098	.25
44.44	45	.0138	.35	.0087	.22
52.36	50	.0117	.297	.0074	.188
61.93	60	.0098	.250	.0064	.162
72.46	70	.0083	.210	.0055	.140
85.47	80	.0070	.177	.0047	.119
101.01	100	.0059	.149	.0040	.102
120.48	120	.0049	.125	.0034	.086
142.86	140	.0041	.105	.0029	.074
166.67	170	.0035	.088	.0025	.063
200.	200	.0029	.074	.0021	.053
230.10	230	.0024	.062	.0018	.046
270.26	270	.0021	.053	.0016	.041
323.	325	.0017	.044	.0014	.036

(B) The Tyler Standard Sieve Series ‡

The Sieve scale has as its base an opening of .0029 inch which is the opening in 200-mesh .0021-inch wire, the standard sieve, as adopted by the U. S. Bureau of Standards, the openings increasing in the ratio of the square root 2 or 1.414.

Where a closer sizing is required column 2 shows the Tyler Standard Screen Scale with intermediate sieves. In this series the sieve openings increase in the ratio of the fourth root of 2 or 1.1892.

* The Standards Report for the Amer. Ceram. Soc., 1928.

† See Bull. Amer. Ceram. Soc., 2 [7], 238-40 (1923).

‡ See Jour. Amer. Ceram. Soc., 6 [3], 563-78 (1923); for Table see p. 346.

<i>Tyler Standard Screen Scale $\sqrt{2}$ or 1.414 (openings in inches)</i>	<i>For closer sizing sieves from .0029 to 1.050-in. ratio $\sqrt{2}$ or 1.189—</i>	<i>Openings (millimeters)</i>	<i>Openings (fractions of inch) (approx.)</i>	<i>Mesh (per lineal inch)</i>	<i>Diameter of wire (inches)</i>
1.050	1.050	26.67	1	—	.148
—	.883	22.43	$\frac{7}{8}$	—	.135
.742	.742	18.85	$\frac{3}{4}$	—	.135
—	.624	15.85	$\frac{5}{8}$	—	.120
.525	.525	13.33	$\frac{1}{2}$	—	.105
—	.441	11.20	$\frac{7}{16}$	—	.105
.371	.371	9.423	$\frac{3}{8}$	—	.092
—	.312	7.925	$\frac{5}{16}$	2½	.088
.263	.263	6.680	$\frac{1}{4}$	3	.070
—	.221	5.613	$\frac{7}{32}$	3½	.065
.185	.185	4.699	$\frac{3}{16}$	4	.065
—	.156	3.962	$\frac{5}{32}$	5	.044
.131	.131	3.327	$\frac{1}{8}$	6	.036
—	.110	2.794	$\frac{7}{64}$	7	.0328
.093	.093	2.362	$\frac{3}{32}$	8	.032
—	.078	1.981	$\frac{5}{64}$	9	.033
.065	.065	1.651	$\frac{1}{16}$	10	.035
—	.055	1.397	—	12	.028
.046	.046	1.168	$\frac{3}{64}$	14	.025
—	.0390	.991	—	16	.0235
.0328	.0328	.833	$\frac{1}{32}$	20	.0172
—	.0276	.701	—	24	.0141
.0232	.0232	.589	—	28	.0125
—	.0195	.495	—	32	.0118
.0164	.0164	.417	$\frac{1}{64}$	35	.0122
—	.0138	.351	—	42	.0100
.0116	.0116	.295	—	48	.0092
—	.0097	.246	—	60	.0070
.0082	.0082	.208	—	65	.0072
—	.0069	.175	—	80	.0056
.0058	.0058	.147	—	100	.0042
—	.0049	.124	—	115	.0038
.0041	.0041	.104	—	150	.0026
—	.0035	.088	—	170	.0024
.0029	.0029	.074	—	200	.0021
Coarser sizing—3- to 1½-inch opening					
—	—	—	3	—	.867
—	—	—	2	—	.192
—	—	—	1½	—	.148

TABLE 56. VOLUME AND WEIGHT CONVERSION TABLE

Van Nostrand's Chemical Annual, J. O. Olsen, Table 234 (1934).

To convert from	Multiply by						
	To Cu. In.	To Cu. Ft.	To Cu. Yd.	To Ft. Oz.	To Pint	To Quart	To Gallon
Cu. In.....	1.00000	0.5787	0.2143	.554112	.034632	.017316	.004329
Cu. Ft.....	1728.00	1.00000	.037037	.957505	59.3442	29.9221	7.48052
Cu. Yd.....	46656.0	27.0000	1.00000	25852.6	1015.79	807.596	201.374
Ft. Oz.....	1.80469	.001044	.033868	1.00000	.069500	.031250	.007813
Pint.....	28.8750	.016710	.061189	16.0000	1.00000	.500000	.125000
Quart.....	57.7500	.033420	.001238	32.0000	2.00000	1.00000	.250000
Gallon.....	231.000	.133681	.004951	128.000	8.00000	4.00000	1.00000
Grain.....	.003954	.022288	.08475	.002191	.021369	.06850	.01712
Oz. Troy.....	1.89805	.001098	.04068	1.05173	.065733	.032867	.008217
Oz. Av.....	1.72999	.001001	.03708	.958608	.059913	.029957	.007489
Lb. Troy.....	22.7766	.013181	.04882	12.6208	.788800	.394400	.098600
Lb. Av.....	27.6799	.016018	.05933	15.3378	.958611	.479306	.119826
CG or Gram.....	.061024	.04531	.01308	.033814	.002113	.001057	.02642
Liter or Kg.....	61.0237	.035315	.001308	33.8140	2.11337	1.05669	.264172
Cu. M.....	61023.7	35.3146	1.30795	33814.0	2113.37	1056.69	264.172

To convert from	Multiply by						
	To Oz. Troy	To Oz. Av.	To Lb. Troy	To Lb. Av.	To CG. or G.	To Ltr. or Kg.	To Cu. M.
Cu. In.....	.526857	.578037	.043905	.036127	16.3871	.016387	.01639
Cu. Ft.....	910.408	998.848	75.8674	62.4280	28316.9	28.3169	.028317
Cu. Yd.....	24581.0	26968.9	2048.42	1685.56	764556	764.556	.764556
Ft. Oz.....	.950813	1.04318	.079234	.065199	29.5736	.029573	.02957
Pint.....	15.2130	16.6908	1.26775	1.04318	.473177	.473177	.04732
Quart.....	30.4260	33.3816	2.53550	2.08635	.946354	.946354	.09463
Gallon.....	121.704	133.527	10.1420	8.34541	3.785.42	3.785.42	.003785
Grain.....	.002083	.002286	.021736	.021428	.064799	.06479	.06479
Oz. Troy.....	1.00000	1.09714	.083333	.068571	31.1035	.031104	.03110
Oz. Av.....	.911457	1.00000	.079355	.062500	28.32495	.028350	.02835
Lb. Troy.....	12.00000	13.1657	1.00000	.822857	373.242	.373242	.03732
Lb. Av.....	14.5833	16.0000	1.21528	1.00000	453.593	.453593	.04536
CG or Gram.....	.032151	.035274	.002679	.002205	1.00000	.001000	.000001
Liter or Kg.....	32.1507	35.2739	2.67923	2.20462	1000.00	1.00000	.001000
Cu. M.....	32150.7	35273.9	2679.23	2204.62	1000000	1000.00	1.00000

Note. The small subnumeral following : zero indicates that the zero is to be taken that number of times; thus, .031428 is equivalent to .0001428

Values used in constructing table:

1 inch = 2.54001 cm.

1 lb av = 453.5926 g

1 lb av = 7000 grains

TABLE 57
TEMPERATURE CONVERSION TABLES
ALBERT SAUVEUR

C	F	C	F	C	F
—273	—459.4	—16.6	2	10.4	51
—268	—450	—16.1	3	11.1	52
—262	—440	—15.5	4	11.5	53
—257	—430	—15.0	5	12.1	54
—251	—420	—14.4	6	12.6	55
—246	—410	—13.9	7	13.2	56
—240	—400	—13.3	8	13.7	57
—234	—390	—12.7	9	14.3	58
—229	—380	—12.2	10	14.8	59
—223	—370	—11.6	11	15.6	60
—218	—360	—11.1	12	16.1	61
—212	—350	—10.5	13	16.6	62
—207	—340	—10.0	14	17.1	63
—201	—330	—9.4	15	17.7	64
—196	—320	—8.8	16	18.2	65
—190	—310	—8.3	17	18.8	66
—184	—300	—7.7	18	19.3	67
—179	—290	—7.2	19	19.9	68
—173	—280	—6.6	20	20.4	69
—169	—273	—6.1	21	21.0	70
—168	—270	—5.5	22	21.5	71
—162	—260	—5.0	23	22.2	72
—157	—250	—4.4	24	22.7	73
—151	—240	—3.9	25	23.3	74
—146	—230	—3.3	26	23.8	75
—140	—220	—2.8	27	24.4	76
—134	—210	—2.2	28	25.0	77
—129	—200	—1.6	29	25.5	78
—123	—190	—1.1	30	26.2	79
—118	—180	—0.6	31	26.8	80
—112	—170	0	32	27.3	81
—107	—160	.5	33	27.7	82
—101	—150	1.1	34	28.2	83
—96	—140	1.6	35	28.8	84
—90	—130	2.2	36	29.3	85
—84	—120	2.7	37	29.9	86
—79	—110	3.3	38	30.4	87
—73	—100	3.8	39	31.0	88
—68	—90	4.4	40	31.5	89
—62	—80	4.9	41	32.1	90
—57	—70	5.5	42	32.6	91
—51	—60	6.0	43	33.3	92
—46	—50	6.6	44	33.8	93
—40	—40	7.1	45	34.4	94
—34	—30	7.7	46	34.9	95
—29	—20	8.2	47	35.5	96
—23	—10	8.8	48	36.1	97
—17.7	0	9.3	49	36.6	98
—17.2	1	9.9	50	37.1	99
—16.6	2	10.4	51	37.7	100

NOTE: The numbers in bold face refer to the temperature either in degrees Centigrade or Fahrenheit which it is desired to convert into the other scale. If converting from Fahrenheit degrees to Centigrade degrees the equivalent temperature will be found in the left column, while if converting from degrees Centigrade to degrees Fahrenheit, the answer will be found in the column on the right.

TEMPERATURE CONVERSION TABLES (Continued)

C			F			C			F			C			F		
38	100	212	260	500	932	538	1000	1832	43	110	230	265	510	950	543	1010	1850
49	120	248	271	520	968	549	1020	1868	54	130	266	276	530	986	554	1030	1886
60	140	284	282	540	1004	560	1040	1904	65	150	302	288	550	1022	565	1050	1922
71	160	320	293	560	1040	571	1060	1940	76	170	338	299	570	1058	576	1070	1958
83	180	356	304	580	1076	582	1080	1976	88	190	374	310	590	1094	587	1090	1994
93	200	392	315	600	1112	593	1100	2012	99	210	410	321	610	1130	598	1110	2030
100	212	413	326	620	1148	604	1120	2048	104	220	428	332	630	1166	609	1130	2066
110	230	446	338	640	1184	615	1140	2084	115	240	464	343	650	1202	620	1150	2102
121	250	482	349	660	1220	626	1160	2120	127	260	500	354	670	1238	631	1170	2138
132	270	518	360	680	1256	637	1180	2156	138	280	536	365	690	1274	642	1190	2174
143	290	554	371	700	1292	648	1200	2192	149	300	572	376	710	1310	653	1210	2210
154	310	590	382	720	1328	659	1220	2228	160	320	608	387	730	1346	664	1230	2246
165	330	626	393	740	1364	670	1240	2264	165	330	626	393	740	1364	670	1240	2264
171	340	644	399	750	1382	675	1250	2282	171	340	644	399	750	1382	675	1250	2282
177	350	662	404	760	1400	681	1260	2300	177	350	662	404	760	1400	681	1260	2300
182	360	680	410	770	1418	686	1270	2318	182	360	680	410	770	1418	686	1270	2318
188	370	698	415	780	1436	692	1280	2336	188	370	698	415	780	1436	692	1280	2336
193	380	716	421	790	1454	697	1290	2354	193	380	716	421	790	1454	697	1290	2354
199	390	734	426	800	1472	704	1300	2372	199	390	734	426	800	1472	704	1300	2372
204	400	752	432	810	1490	708	1310	2390	204	400	752	432	810	1490	708	1310	2390
210	410	770	438	820	1508	715	1320	2408	210	410	770	438	820	1508	715	1320	2408
215	420	788	443	830	1526	719	1330	2426	215	420	788	443	830	1526	719	1330	2426
221	430	806	449	840	1544	726	1340	2444	221	430	806	449	840	1544	726	1340	2444
226	440	824	454	850	1562	734	1350	2462	226	440	824	454	850	1562	734	1350	2462
232	450	842	460	860	1580	737	1360	2480	232	450	842	460	860	1580	737	1360	2480
238	460	860	465	870	1598	741	1370	2498	238	460	860	465	870	1598	741	1370	2498
243	470	878	471	880	1616	748	1380	2516	243	470	878	471	880	1616	748	1380	2516
249	480	896	476	890	1634	752	1390	2534	249	480	896	476	890	1634	752	1390	2534
254	490	914	482	900	1652	760	1400	2552	254	490	914	482	900	1652	760	1400	2552
260	500	932	487	910	1670	765	1410	2570	260	500	932	487	910	1670	765	1410	2570
			493	920	1688	771	1420	2588				493	920	1688	771	1420	2588
			498	930	1706	776	1430	2606				498	930	1706	776	1430	2606
			504	940	1724	782	1440	2624				504	940	1724	782	1440	2624
			510	950	1742	787	1450	2642				510	950	1742	787	1450	2642
			515	960	1760	793	1460	2660				515	960	1760	793	1460	2660
			520	970	1778	798	1470	2678				520	970	1778	798	1470	2678
			526	980	1796	804	1480	2696				526	980	1796	804	1480	2696
			532	990	1814	809	1490	2714				532	990	1814	809	1490	2714
			538	1000	1832	815	1500	2732				538	1000	1832	815	1500	2732

TEMPERATURE CONVERSION TABLES (Continued)

C		F	C		F	C		F
815	1500	2732	1093	2000	3632	1371	2500	4532
820	1510	2750	1098	2010	3650	1376	2510	4550
827	1520	2768	1104	2020	3668	1382	2520	4568
831	1530	2786	1109	2030	3686	1387	2530	4586
838	1540	2804	1115	2040	3704	1393	2540	4604
842	1550	2822	1120	2050	3722	1398	2550	4622
849	1560	2840	1126	2060	3740	1404	2560	4640
853	1570	2858	1131	2070	3758	1409	2570	4658
860	1580	2876	1137	2080	3776	1415	2580	4676
864	1590	2894	1142	2090	3794	1420	2590	4694
871	1600	2912	1149	2100	3812	1427	2600	4712
876	1610	2930	1154	2110	3830	1432	2610	4730
882	1620	2948	1160	2120	3848	1438	2620	4748
887	1630	2966	1165	2130	3866	1443	2630	4766
893	1640	2984	1171	2140	3884	1449	2640	4784
898	1650	3002	1176	2150	3902	1454	2650	4802
904	1660	3020	1182	2160	3920	1460	2660	4820
909	1670	3038	1187	2170	3938	1465	2670	4838
915	1680	3056	1193	2180	3956	1471	2680	4856
920	1690	3074	1198	2190	3974	1476	2690	4874
926	1700	3092	1204	2200	3992	1483	2700	4892
931	1710	3110	1209	2210	4010	1488	2710	4910
937	1720	3128	1215	2220	4028	1494	2720	4928
942	1730	3146	1220	2230	4046	1499	2730	4946
948	1740	3164	1226	2240	4064	1505	2740	4964
953	1750	3182	1231	2250	4082	1510	2750	4982
959	1760	3200	1237	2260	4100	1516	2760	5000
964	1770	3218	1242	2270	4118	1521	2770	5018
970	1780	3236	1248	2280	4136	1527	2780	5036
975	1790	3254	1253	2290	4154	1532	2790	5054
981	1800	3272	1259	2300	4172	1538	2800	5072
986	1810	3290	1264	2310	4190	1543	2810	5090
992	1820	3308	1270	2320	4208	1549	2820	5108
997	1830	3326	1275	2330	4226	1554	2830	5126
1003	1840	3344	1281	2340	4244	1560	2840	5144
1008	1850	3362	1286	2350	4262	1565	2850	5162
1014	1860	3380	1292	2360	4280	1571	2860	5180
1019	1870	3398	1297	2370	4298	1576	2870	5198
1025	1880	3416	1303	2380	4316	1582	2880	5216
1030	1890	3434	1308	2390	4334	1587	2890	5234
1036	1900	3452	1315	2400	4352	1593	2900	5252
1041	1910	3470	1320	2410	4370	1598	2910	5270
1047	1920	3488	1326	2420	4388	1604	2920	5288
1052	1930	3506	1331	2430	4406	1609	2930	5306
1058	1940	3524	1337	2440	4424	1615	2940	5324
1063	1950	3542	1342	2450	4442	1620	2950	5342
1069	1960	3560	1348	2460	4460	1626	2960	5360
1074	1970	3578	1353	2470	4478	1631	2970	5378
1080	1980	3596	1359	2480	4496	1637	2980	5396
1085	1990	3614	1364	2490	4514	1642	2990	5414
1093	2000	3632	1371	2500	4532	1649	3000	5432

TABLE 58

APPROXIMATE TEMPERATURE BY COLOR

	<i>Fahr.</i>	<i>Cent.</i>
First visible red.....	900	482
Dull red.....	1175	635
Bright red.....	1550	843
Orange.....	1725	941
White.....	2200	1204
Dazzling white.....	2732	1500

TABLE 59

COMPARATIVE HEAT VALUES OF COAL, OIL AND GAS

<i>Calorific Value of Coal B.T.U. per lb.</i>	<i>Quantity of Coal Equal to 1 bbl. of Oil Pounds</i>	<i>Quantity of Oil Equal to 1 Short Ton of Coal Barrels</i>	<i>Quantity of Coal Equal to 1000 cu. ft. of Gas Pounds</i>	<i>Quantity of Gas Equal to 1 Short Ton of Coal Thousands of Feet</i>
10,000	620	3.23	100	20
11,000	564	3.55	91	22
12,000	517	3.87	83	24
13,000	477	4.19	77	26
14,000	443	4.52	71	28
15,000	413	4.84	67	30

* Bureau of Mines Bulletin. "Efficiency in the Use of Oil Fuel," by J. M. Wadsworth.

TABLE 60
FUEL CONSUMPTION FOR MAINTAINING FURNACE TEMPERATURE

Furnace Temper- ature Degrees F.	MINIMUM QUANTITY OF FUEL PER MILLION B.T.U./HR. HEAT LOSS					
	Gallons of Oil Per Hr.	Pounds Coal Per Hr.	Cu. Ft. Natural Gas Per Hr.	Cu. Ft. of Producer Gas Per Hr.	K.W. Hours Per Hr.	H.P. Hours Per Hr.
1200	10.5	94	1550	12200	293	392
1400	11.2	101	1680	13500	293	392
1600	12.0	107	1800	15400	293	392
1800	13.0	116	1980	17900	293	392
2000	14.2	128	2190	21800	293	392
2200	15.7	142	2460	27800	293	392
2400	17.6	159	2840	38500	293	392
2600	20.1	180	3370	62500	293	392

The above figures are based on complete combustion, no excess air; combustion air not preheated.

The tables are based on the following figures for higher calorific values of the fuels:

Oil = 135,000 B.T.U./Gal.
 Coal = 14,400 B.T.U./Pound
 Natural Gas = 960 B.T.U./Cu. Ft.
 Producer Gas = 137 B.T.U./Cu. Ft.
 1 K.W. Hr. = 3417 B.T.U.
 1 H.P. Hr. = 2547 B.T.U.

* Compiled from Trinks, "Industrial Furnaces."

TABLE 61
CALORIFIC VALUE OF FUEL OILS

Kind of Oil	Specific Gravity	B.T.U. Per Pound
California, Kern.....	0.9589	18,840
California, Coalinga.....	0.927	17,117
California, Bakersfield.....	0.975	17,600
California, Whittier.....	.9944	18,507
Pennsylvania.....	0.886	19,210
West Virginia.....	0.841	21,240
Texas, Beaumont.....	0.924	19,060
Texas, Sabine.....	0.937	18,662
Russia, Baku.....	0.884	20,691
Mexico.....	0.921	18,840
Austria, Galicia.....	0.870	18,416

Bureau of Mines Bulletin, "Efficiency in the Use of Oil Fuel," by J. M. Wadsworth.

TABLE 62
EQUIVALENT WEIGHTS

<i>Oxide, etc.</i>	<i>Formula</i>	<i>Equivalent Weight</i>
Aluminum fluoride.....	AlF_3	84.0
Aluminum oxide.....	Al_2O_3	101.9
Antimony oxide.....	Sb_2O_3	291.5
Barium oxide.....	BaO	153.4
Boric oxide.....	B_2O_3	69.6
Calcium fluoride.....	CaF_2	78.1
Calcium oxide.....	CaO	56.1
Cobalt oxide.....	CoO	74.9
Cobalto cobaltic oxide.....	Co_2O_3	240.8
Ferrie oxide.....	Fe_2O_3	159.7
Ferrous oxide.....	FeO	71.8
Fluorine	F_2	38.0
Lead oxide.....	PbO	223.2
Magnesium oxide.....	MgO	40.3
Manganese dioxide.....	MnO_2	86.9
Manganous oxide.....	MnO	70.9
Potassium oxide.....	K_2O	94.2
Red lead.....	Pb_3O_4	685.7
Silicon dioxide.....	SiO_2	60.1
Sodium fluoride.....	NaF	42.0
Sodium oxide.....	Na_2O	62.0
Tin oxide.....	SnO_2	150.7
Titanium oxide.....	TiO_2	79.9
Zinc oxide.....	ZnO	81.4
Zirconium oxide.....	ZrO_2	123.2

The molecular weights (formula weights) of materials are given in Table 1.

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